

BORON HYDRIDE CHEMISTRY OF N-SUBSTITUTED-
IMINOTRIPHENYLPHOSPHORANES

By

WILLIAM KEITH HOLLEY

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1986

ACKNOWLEDGEMENTS

The author wishes to express his deepest appreciation to Dr. George E. Ryschkewitsch, for his guidance, supervision and encouragement during the period of this research program. The interaction with him, both as a student and a friend, will always be remembered.

The author wishes to express his gratitude to the members of his advisory committee for their help and support. He is also thankful to Donald S. Swieter for his help throughout this study.

The author would also like to thank Dr. W.S. Brey and his associates for obtaining the high field B^{11} , P^{31} and H^1 nmr spectra reported in this study. Special thanks are due to Dr. R.W. King for obtaining the mass spectra in this study and for the instrumental instruction that the author received from him. The author extends thanks to Mr. Mel Courtney for obtaining the elemental analyses used in this study. The author would also like to thank Dr. G.J. Palenik for obtaining the crystal structures reported in this study.

The author gratefully acknowledges the financial support of this research by the Department of Chemistry, University of Florida.

Finally, the author expresses his gratitude to his parents for their support and encouragement during the course of study and to Dr. Donald F. Clemens for getting him started.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS	ii
LIST OF TABLES	vi
LIST OF FIGURES	ix
ABSTRACT	xii
CHAPTERS	
I INTRODUCTION	1
II MATERIALS AND PROCEDURES	13
Materials	13
Procedures	15
III SYNTHESSES OF BORANE ADDUCTS AND BORON CATIONS	19
Syntheses of Borane Adducts	21
Syntheses of Boron Cations	30
IV PHYSICAL, CHEMICAL AND SPECTRAL PROPERTIES OF BORANE ADDUCTS AND BORON CATIONS	36
Physical and Chemical Properties	36
Spectral Properties	46
V DISCUSSION ON SYNTHESSES OF BORANE ADDUCTS AND BORON CATIONS	98
Syntheses of Borane Adducts	98
Synthesis of Boron Cations	106
VI MEASUREMENT OF EQUILIBRIUM CONSTANTS FOR THE EXCHANGE OF BH_3 BETWEEN N-ALKYLMINO-TRIPHENYLPHOSPHORANES AND BORANE ADDUCTS OF TRIMETHYLAMINE AND 4-METHYLPYRIDINE	116
Preparation to Measure Exchange of BH_3 Between N-Methyliminotriphenylphosphorane and Trimethylamine Borane	116

	Results and Treatment of Data	119
	Discussion and Errors	138
VII	DETERMINATION OF THE AMOUNT OF PI-BONDING BETWEEN PHOSPHORUS AND NITROGEN	149
	Pi-Bond Character Measured from Phosphorus-Nitrogen Bond Distances	149
	Pi-Bond Character Measured from P^{31} NMR Chemical Shifts	169
	Conclusion	177
VIII	REDUCTION OF IMINOTRIPHENYLPHOSPHORANE AND N,N-DIMETHYLAMINOTRIPHENYLPHOSPHONIUM ION	178
	Reaction of Iminotriphenylphosphorane With Tetra-n-Butyl-Ammonium Boro- hydride	179
	Reaction of N,N-Dimethylaminotriphenyl- phosphonium Iodide With Sodium Dimethylaminoborohydride	193
	Reaction of N,N-Dimethylaminotriphenyl- phosphonium Iodide With Lithium Borohydride	196
	Conclusion	203
IX	SUMMARY	207
APPENDIX	COMPUTER PROGRAM USED IN CALCULATION OF n_{π} FOR N-ETHYLIMINOTRIPHENYLPHOSPHORANE	211
REFERENCES	213
BIOGRAPHICAL SKETCH	219

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Yields and Melting Points of N-Alkylimino-and β -N-Substituted-Aminoimino-triphenylphosphorane Boranes	24
2. Analyses of N-Alkylimino-and β -N-Substituted-Aminoimino-Triphenylphosphorane Boranes	25
3. Comparison of the Two Methods Used to Synthesize Borane Adducts	31
4. Yields and Melting Points of Bis(N-Alkylimino-triphenylphosphorane) Boronium Iodides	34
5. Analyses of Bis(N-Alkyliminotriphenylphosphorane) Boronium Iodides	34
6. Infrared Data of N-Alkylimino-and β -N-Substituted-Aminoimino-Triphenylphosphoranes	50
7. Infrared Data of N-Alkylimino-and β -N-Substituted-Aminoimino-Triphenylphosphorane Boranes	51
8. Infrared Data of Bis-(N-Alkyliminotriphenylphosphorane) Boronium Iodides	53
9. Mass Intensity Data for N-Ethyliminotriphenylphosphorane Borane	63
10. Proton and P^{31} NMR Data of N-Alkylimino-and β -N-Substituted-Aminoimino-Triphenylphosphoranes	68
11. Proton and P^{31} NMR Data of N-Alkylimino and β -N-Substituted-Aminoimino-Triphenylphosphorane Boranes	70
12. Proton and P^{31} NMR Data of Bis-(N-Alkylimino-triphenylphosphorane) BH_2I^- Salts	72
13. B^{11} NMR Data of Borane Adducts and Boron Cations	73

<u>Table</u>	<u>Page</u>
14. Line Positions and Intensities for the A_2X_2 Case	77
15. Line Positions of the α Protons	79
16. Line Positions of the B Part	83
17. Starting Concentrations of Reactants in the Exchange of BH_3 Between N-Alkylimino-triphenylphosphorane and Trimethylamine Borane	118
18. Starting Concentrations of Reactants in the Exchange of BH_3 Between N-Alkylimino-triphenylphosphorane and 4-Methylpyridine Borane	118
19. P^{31} and B^{11} NMR Data for Exchange of BH_3	120
20. H^1 NMR Data for Exchange of BH_3	121
21. Equilibrium Constants for Exchange of BH_3	134
22. Equilibrium Constants for Exchange of BH_3	134
23. H^1 NMR Data for Exchange of BH_3	135
24. Calculated Values of K_{TP} Using Equation (6.7) . .	139
25. Enthalpies and Entropies of Reaction	145
26. Bond Lengths in N-Methyliminotriphenylphosphorane Borane	152
27. Bond Angles in N-Methyliminotriphenylphosphorane Borane	153
28. Bond Lengths in N,N-Dimethylaminotriphenylphosphonium Tetrafluoroborate	159
29. Bond Angles in N,N-Dimethylaminotriphenylphosphonium Tetrafluoroborate	162
30. Planar Angles in N-Methyliminotriphenylphosphorane Borane	167
31. Planar Angles in N,N-Dimethylaminotriphenylphosphonium Ions	167
32. Parameters Used in and Results of Equation (7.2) for $(C_6H_5)_3PM$	173

<u>Table</u>	<u>Page</u>
33. Change in Pi-Bonding on Coordination of Phosphoranes by BH_3	174
34. Effect of Changing Angles EA and EP on the Value of α_1 for $\text{M} = \text{N}(\text{CH}_3)\text{BH}_3$	176
35. Infrared Data of Iminotriphenylphosphorane and Product from Reaction with Tetra-n-Butyl- Ammonium Borohydride	183
36. C^{13} NMR Data of Solid Obtained by Reaction of Iminotriphenylphosphorane with Tetra-n-Butyl- Ammonium Borohydride	186
37. Mass Intensity Data of Solid Obtained by Reaction of Iminotriphenylphosphorane with Tetra-n-Butyl-Ammonium Borohydride	189
38. Mass Balance	200
39. Possible Reaction Products Containing Boron . . .	202

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Apparatus for synthesis of phosphoranes	20
2. Apparatus for synthesis of borane adducts	28
3. Infrared spectrum of N-ethyliminotriphenylphosphorane	54
4. Infrared spectrum of β -N-dimethylaminoimino triphenylphosphorane	55
5. Infrared spectrum of N-tert-butyliminotriphenylphosphorane borane	57
6. Infrared spectrum of β -N-phenylaminoimino-triphenylphosphorane borane	58
7. Infrared spectrum of bis-(N-methyliminotriphenylphosphorane) boronium iodide	59
8. Mass spectrum of N-ethyliminotriphenylphosphorane borane	62
9. Symmetry and coupling constants of the A_2B_2 case	75
10. Expansion of α protons in H^1 nmr spectrum of N-n-propyliminotriphenylphosphorane borane . . .	78
11. Expansion of β protons in H^1 nmr spectrum of N-n-propyliminotriphenylphosphorane borane . . .	81
12. Expansion of β protons, decoupled from methyl protons, in H^1 spectrum of N-n-propyliminotriphenylphosphorane borane	82
13. H^1 nmr spectrum of N-n-propyliminotriphenylphosphorane	84
14. H^1 nmr spectrum of N-n-propyliminotriphenylphosphorane borane	85

<u>Figure</u>	<u>Page</u>
15. H^1 nmr spectrum of bis-(N-ethyliminotriphenylphosphorane) boronium iodide	87
16. Proton decoupled B^{11} nmr spectrum of N-methyliminotriphenylphosphorane borane	90
17. Proton coupled B^{11} nmr spectrum of N-methyliminotriphenylphosphorane borane	91
18. Proton coupled B^{11} nmr spectrum of N-ethyliminotriphenylphosphorane borane	92
19. Proton coupled B^{11} nmr spectrum of β -N-phenylaminoiminotriphenylphosphorane borane	93
20. Proton coupled B^{11} nmr spectrum of β -N-methyl, phenylaminoiminotriphenylphosphorane borane	94
21. Proton coupled B^{11} nmr spectrum of bis-(N-n-propyliminotriphenylphosphorane)boronium iodide	95
22. Proton decoupled B^{11} nmr spectrum of bis(N-n-propyliminotriphenylphosphorane)boronium iodide	96
23. HOMO-LUMO interaction in $Sn2$ mechanism	99
24. HOMO-LUMO interaction in $Sn1$ mechanism	100
25. Transition state for $Sn2$ reaction on $(C_6H_5)_3PNRBH_2I$	109
26. Transition state for trimethylamine displacement in (trimethylamine)(pyridine)boronium iodide . .	114
27. Transition state for trimethylamine displacement in (trimethylamine)(N-n-propyliminotriphenylphosphorane)boronium iodide	114
28. Expansion of H^1 nmr spectrum for exchange of BH_3 between N-methyliminotriphenylphosphorane and trimethylamine borane at 25°	123
29. Expansion of H^1 nmr spectrum for exchange of BH_3 between N-methyliminotriphenylphosphorane and trimethylamine borane at 50°	124

<u>Figure</u>	<u>Page</u>
30. Expansion of methyl resonances of phosphorane and phosphorane borane in H^1 nmr spectrum for exchange of BH_3 between N-methyliminotriphenylphosphorane and 4-methylpyridine borane at 50°	126
31. Expansion of methyl resonances of 4-methylpyridine borane and 4-methylpyridine in H^1 nmr spectrum for exchange of BH_3 between N-methyliminotriphenylphosphorane and 4-methylpyridine borane at 50°	127
32. Expansion of H^1 nmr spectrum for exchange of BH_3 between N-n-propyliminotriphenylphosphorane and 4-methylpyridine borane	129
33. P^{31} nmr spectrum for exchange of BH_3 between N-ethyliminotriphenylphosphorane and 4-methylpyridine borane at 25°	131
34. Proton decoupled B^{11} nmr spectrum for exchange of BH_3 between N-n-propyliminotriphenylphosphorane and trimethylamine borane at 50°	133
35. Expansion of H^1 spectrum for exchange of BH_3 between 4-methylpyridine and trimethylamine borane at 25°	137
36. Structure of N-methyliminotriphenylphosphorane borane	151
37. Structure of cation 1 in N,N-dimethylaminotriphenylphosphonium tetrafluoroborate	156
38. Structure of cation 2 in N,N-dimethylaminotriphenylphosphonium tetrafluoroborate	157
39. Structures of tetrafluoroborate anion in N,N-dimethylaminotriphenylphosphonium tetrafluoroborate	158
40. Infrared spectrum of $[(C_6H_5)_3PN]_2BH$	182
41. C^{13} nmr spectrum of $[(C_6H_5)_3PN]_2BH$	185
42. Mass spectrum of $[(C_6H_5)_3PN]_2BH$	188

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

BORON HYDRIDE CHEMISTRY OF N-SUBSTITUTED-
IMINOTRIPHENYLPHOSPHORANES

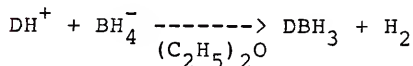
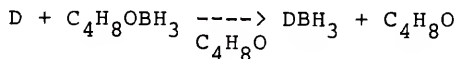
By

William Keith Holley

December, 1986

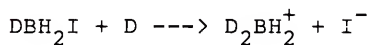
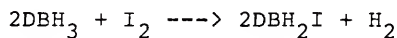
Chairman: Professor G.E. Ryschkewitsch
Major Department: Chemistry

Borane adducts of N-substituted-iminotriphenylphos-
phoranes were prepared by two different general synthetic
methods. The first method involved displacement of tetra-
hydrofuran from borane tetrahydrofuran complex. The second
method employed in situ generation of diborane by reaction
of lithium borohydride with N-substituted-aminotriphenyl-
phosphonium bromides in diethyl ether. The two methods are
represented by the following equations:



where D = a N-substituted-iminotriphenylphosphorane.

A number of symmetrical cations were prepared which contain a BH_2^+ group coordinated with N-alkyliminotriphenylphosphoranes. They were synthesized by iodination of the corresponding borane adduct followed by bimolecular nucleophilic substitution. The reaction steps are represented by the following equations:



where D = a N-alkyliminotriphenylphosphorane.

Physical, chemical and spectral properties of the borane adducts and boron cations, namely thermal and hydrolytic stability, infrared and nmr spectra were discussed in detail. In addition, the stability of the cations towards Ag(I) and borohydride ions was studied.

Discussion on the synthetic methods includes steric and electronic factors of the nucleophiles and substrates, reaction mechanisms and comparison of reactivities of boranes and boron cations, containing phosphoranes as ligands, with the corresponding amine substituted entities. Phosphoranes appear to be better nucleophiles than amines, and phosphorane iodoboranes react faster than trimethylamine iodoborane. Steric and electronic factors appear to play an important role in defining the reactivity of the iodoborane

adducts. Comparison of the two methods to prepare borane adducts showed that the second method was preferred.

Relative basicities of N-alkyliminotriphenylphosphoranes were determined by measuring equilibrium constants for exchange of BH_3 between phosphoranes and borane adducts of trimethylamine and 4-methylpyridine. It was found that the phosphoranes are less basic than trimethylamine.

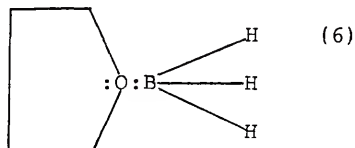
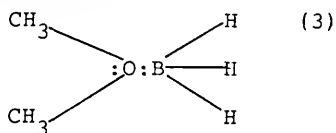
The amount of pi-bonding between phosphorus and nitrogen was determined by crystallographic and P^{31} nmr data.

Reduction of iminotriphenylphosphorane and N,N-dimethylaminotriphenylphosphonium ion by different reducing agents was studied in detail. A new product was isolated and characterized from the reaction of tetra-n-butylammonium borohydride with iminotriphenylphosphorane. The compound was identified as $[(\text{C}_6\text{H}_5)_3\text{PN}]_2\text{BH}$.

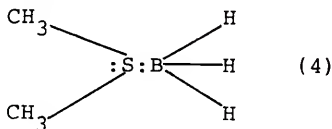
CHAPTER I
INTRODUCTION

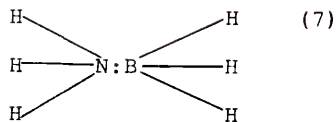
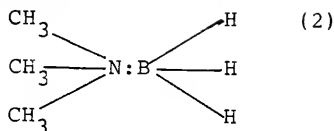
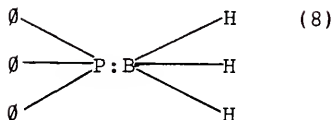
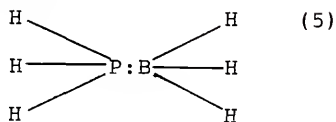
Adducts of diborane (1) are characterized by having an electron pair donor coordinated to a BH_3 group. Burg and Schlesinger (2) isolated the first adducts of diborane, OCBH_3 and trimethylamine borane. Since that time a large variety of borane adducts has been synthesized employing oxygen (3), nitrogen (2), sulfur (4), and phosphorus (5) as electron donors. Their examples are represented as follows:

Ether Boranes



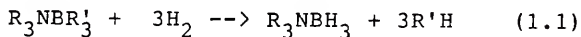
Thioether Boranes



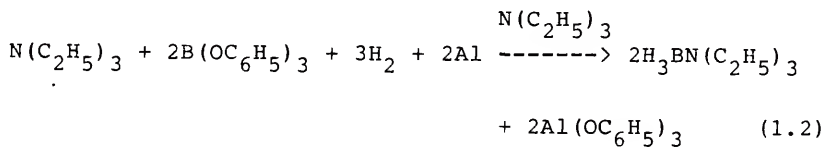
Amine BoranesPhosphine Boranes

The most common route to borane adducts is direct combination of the donor and diborane at low temperature (2-6).

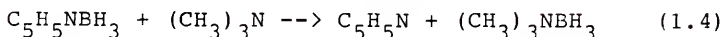
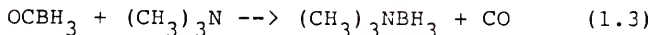
The class of borane adducts which has received the largest amount of attention is the amine boranes. There are numerous different procedures for synthesizing amine boranes. Koster obtained them by high pressure hydrogenolysis of amine trialkylboranes (9).



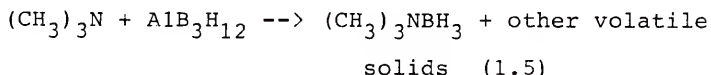
Ashby and Foster (10) prepared them by reduction of alkoxyboranes with aluminum and hydrogen in an amine solvent.



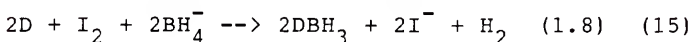
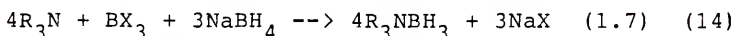
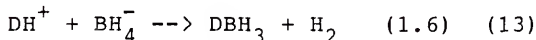
Schlesinger et al. (2,11) produced them by displacement of a donor attached to BH_3 .



Schlesinger et al. (12) also obtained amine boranes by reaction of an amine with an aluminum boron hydride.



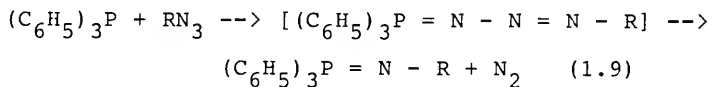
Other procedures employ in situ generation of diborane in the presence of an amine as follows:



Iminotriphenylphosphoranes represent an important class of reactive intermediates in organic synthesis. Imino-triphenylphosphoranes contain the basic structure of $(\text{C}_6\text{H}_5)_3\text{P} = \text{N-R}$. The nomenclature adopted in this text for these compounds follows the rules agreed upon by The Organic Division's Advisory Committee on the Nomenclature of Organic Phosphorus Compounds (16). The parent structure on which the names are based is taken as phosphorane, H_5P . In

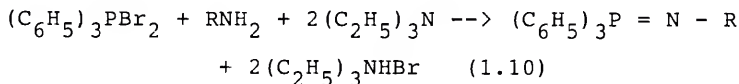
general cases, the compounds may be referred to as imino-triphenylphosphoranes or phosphoranes for brevity.

The first iminotriphenylphosphoranes were made by Staudinger et al. (17,18) by reacting triphenylphosphine with an organic azide.

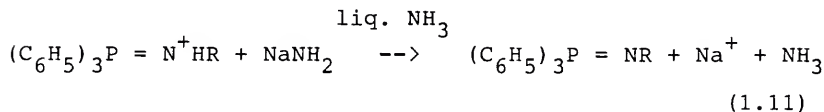


Since that time a number of compounds with different R groups have been reported (19-22). The preparations of these compounds involve dehydrohalogenation of the corresponding aminotriphenylphosphonium salts.

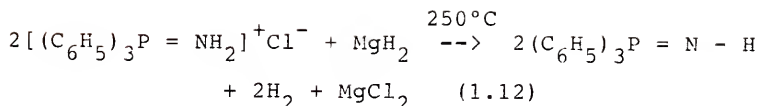
Horner and Oediger (21) carried out the dehydrohalogenation with triethylamine.



Two separate research groups (19,23) have described the dehydrohalogenation with sodamide in liquid ammonia.



Sisler et al. (24) have dehydrohalogenated aminotriphenylphosphonium chloride with magnesium hydride.



During the current investigation, a new compound of the aforementioned class, β -N-phenylaminoiminotriphenylphosphorane, was synthesized and characterized.

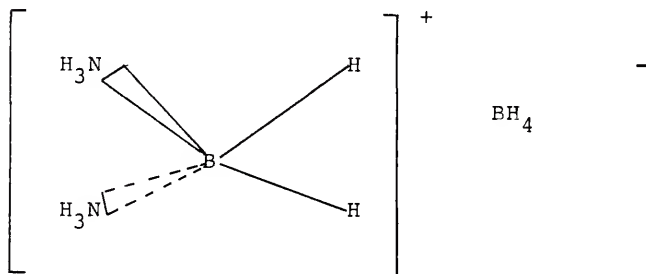
Although several BF_3 adducts of the iminotriphenylphosphoranes have been reported in the literature (25,26), the only BH_3 adduct mentioned is that of the parent compound, iminotriphenylphosphorane (25). Therefore, one of the objectives of the present work was to prepare and characterize a series of new borane adducts employing N-substituted-iminotriphenylphosphoranes as ligands.

Little or no information on the IR (19), H^1 -nmr (20,27), and P^{31} -nmr spectra of the iminotriphenylphosphoranes used in this study was available. It was necessary, therefore, during the course of this investigation, to record infrared and nmr spectra on all the iminotriphenylphosphoranes used in the current study.

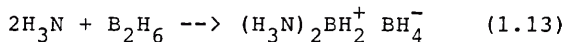
Borane adducts are a basic starting material to other boron compounds. Closely related to borane adducts, boron cations constitute an important class of boron compounds. Boron cations containing only one boron atom can be considered as coordination compounds of boron (III). Therefore, when less than three negatively charged ligands are complexed to boron, a positively charged species is formed.

By varying the number of negatively charged ligands, mono-, di-, and tri- cations are possible.

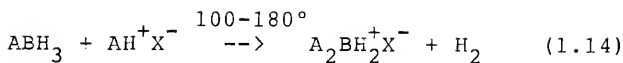
Boron cation chemistry developed after the elucidation of the structure of the diammoniate of diborane (28). It was found that the diammoniate of diborane is the tetrahydroborate salt of the boron cation, diaminedihydroboron(+1).



Since this time a number of boron cations have been reported in the literature (29,30). The majority of the boron cations reported contain a single positive charge. There are several general methods for the preparation of singly charged cations. A small number of boron cations have been prepared by unsymmetrical cleavage of diborane (28,31).

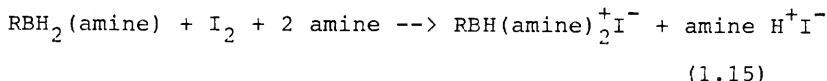


Miller and Muettterties (32) prepared boron cations by reaction of borane adducts with onium salts of large anions.

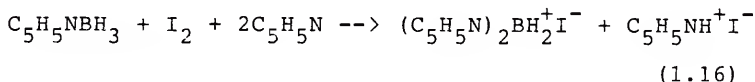


A = tertiary amine X = halogen

In general, boron cations are formed by the displacement of an anion from an amine halo borane by a neutral base. This method was pioneered by Douglass et al. (33,34) to prepare boronium ions of the type $(\text{amine})_2BRH^+$ where R represents organo groups.



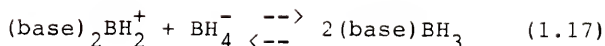
The method was further developed by Ryschkewitsch (35) to prepare the $(C_5H_5N)_2BH_2^+$ cation.



Since that time a number of boron cations of the type $(\text{base})(\text{base}')BH_2^+$ where $\text{base}=\text{base}'$ or $\text{base}\neq\text{base}'$ have been prepared by the aforementioned method (29,36,37).

Another objective of the present work was to prepare a series of boron cations of the type $(\text{base})(\text{base}')BH_2^+$ employing N-alkyliminotriphenylphosphoranes as the bases.

Boron cations of the type $(\text{base})_2BH_2^+$ in the presence of borohydride ion can interconvert to borane adducts.



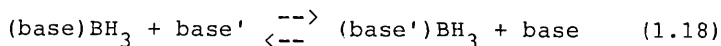
The more thermodynamically stable product should result. For example, the borohydride salts of bis(monomethylamine)boronium cation and bis(dimethylamine)boronium cation do not transform into the corresponding amine boranes in solution (38). However, the BH_2^+ cation derived from tert-butylamine reacts with lithium borohydride to produce tert-butylamine borane (39).

A third objective of the present work was to investigate the stabilities of the bis(alkyliminotriphenylphosphorane) boronium cations in the presence of borohydride ion.

Iminotriphenylphosphoranes have been shown to be basic materials. They act as Lewis bases to form adducts (25,26) and as Bronsted bases reacting with hydrogen halides (17,18,40). Information on their relative base strengths is scant. It has been reported that the alkylaminotriphenylphosphonium halides cannot be deprotonated by triethylamine (21,41).

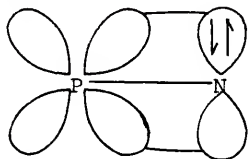
Johnson and Wong (42) determined pK_a values of the hydrochloride salts of a series of N-(substituted-phenyl)-iminotriphenylphosphoranes by potentiometric titrations in 95% ethanol solution. Their results show that the N-(substituted-phenyl)-iminotriphenylphosphoranes are much weaker bases than ammonia.

Graham and Stone (43) used BF_3 and BH_3 as reference acids to measure the relative base strengths of some thioethers, phosphines, and amines. The base strengths were determined by measuring equilibrium constants for exchange of BH_3 between two different donors in the gas phase.

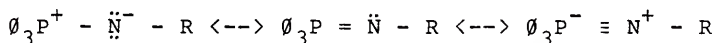


A fourth objective of the present work was to study the relative basicities of the alkyliminotriphenylphosphoranes. This was done by measuring equilibrium constants for exchange of BH_3 between the alkyliminotriphenylphosphoranes and ordinary amines.

Iminotriphenylphosphoranes exhibit varying amounts of multiple bonding between phosphorus and nitrogen. This bonding is referred to as $d_{\pi}-p_{\pi}$ bonding in which filled 2p orbitals on nitrogen overlap with empty 3d orbitals on phosphorus.



Three different resonance structures can be drawn to represent bonding in the iminotriphenylphosphoranes.



Craig and Paddock (44) published an excellent discussion on electron distribution in cyclic $d_{\pi}-p_{\pi}$ systems. They attempted to correlate the amount of $d_{\pi}-p_{\pi}$ overlap in cyclic phosphazenes by comparing two different physical properties. Phosphorus-nitrogen bond lengths are compared to the P-N bond length in phosphoramidate ion of 1.78\AA (45) and to the sum of single covalent radii of 1.76\AA . Also, the dissociation energies for P-N are compared to a calculated value of 65 kcal/mole (for a single bond) and an experimental value of 66.8 kcal/mole in trisdiethylamido-phosphine (46).

Claydon, Fowell, and Mortimer (47) determined the P-N dissociation energy in N-ethyliminotriphenylphosphorane to be approximately 125 kcal/mole. This would attribute approximately 58 kcal/mole of energy to $d_{\pi}-p_{\pi}$ interaction in N-ethyliminotriphenylphosphorane.

Letcher and Van Wazer (48) present an elaborate quantum mechanical theory to describe $P^{31}\text{nmr}$ chemical shifts. They demonstrate by examples that, to a first approximation, P^{31} chemical shifts are determined by the number and kind of atoms immediately adjacent to the phosphorus in the molecule. According to this theory, the P^{31} chemical shift, δ , is attributable to two additive quantities. One involves the occupation of the p orbitals on phosphorus, and the other involves occupation of the d orbitals. It was concluded that molecular structures based on triply and quadruply connected phosphorus have σ bonding involving only

s and p orbitals and that the d orbitals are reserved for π bonding. For compounds based on quadruply connected phosphorus, the P^{31} chemical shift, δ , referenced to 85% phosphoric acid, is given by

$$\delta = 11,828.5 - 7940\alpha_1 - 149n_\pi$$

where n_π is the total occupation of the d_π orbitals of phosphorus in electronic charge per phosphorus atom, and δ is the P^{31} chemical shift in ppm which would be observed if the occupation of the d_π orbitals of the phosphorus were zero. A short computer program, which takes into account the electronegativities of the groups attached to phosphorus and the group bond angles around the phosphorus, is used to calculate α_1 . By rearranging the above equation, n_π can be solved for.

$$n_\pi = \frac{-\delta + 11,828.5 - 7940\alpha_1}{149}$$

A final objective of the current investigation was to determine the amount of π bonding between phosphorus and nitrogen in the N-substituted-iminotriphenylphosphoranes and their borane adducts by a combination of crystallographic and P^{31} nmr data.

Phosphorus atoms in molecules can exist in a number of oxidation states. The most stable oxidation state of

phosphorus in aqueous solution is +5. Iminotriphenylphosphoranes contain phosphorus in the oxidation state of +5. Reduction of the +5 oxidation state of phosphorus even in non-aqueous solutions is difficult. A subsidiary objective of the current research program was to investigate the possibility of reduction of iminotriphenylphosphorane and N,N-dimethylaminotriphenylphosphonium ion with hydride ion. Hydride ion was chosen because it is a strong reducing agent and should be a good nucleophile toward phosphorus.

CHAPTER II
MATERIALS AND PROCEDURES

Materials

Boranes

Borane-tetrahydrofuran complex was obtained from Aldrich Chemical Company and was used without further purification. Trimethylamine borane was obtained from Callery Chemical Company. Dimethylamine borane was purchased from Aldrich Chemical Company. The compound 4-methylpyridine borane was synthesized from 4-methylpyridine and borane-tetrahydrofuran complex. The amine boranes and 4-methylpyridine borane were sublimed prior to use.

Amines

Amines were purchased from various commercial sources--namely, Eastman Organic Chemicals, Aldrich Chemical Company, and Matheson Gas Products. Amines were distilled prior to use. The compound 4-methylpyridine was obtained from Eastman Organic Chemicals and was distilled from barium oxide.

Hydrazines

The various hydrazines purchased were unsymmetrical dimethylhydrazine from FMC Corporation, phenylhydrazine from Fisher Scientific Company, and N-methyl,N-phenylhydrazine from Fluka Chemical Corporation. The hydrazines were used without further purification.

Triphenylphosphine

Triphenylphosphine was obtained from Aldrich Chemical Company, Peninsular ChemResearch, and Matheson Coleman and Bell and was used without further purification.

Halogens

Iodine was purchased from Mallinckrodt Chemical Company and bromine from Fisher Scientific Company.

N-substituted-Iminotriphenylphosphoranes

The N-substituted-iminotriphenylphosphoranes were prepared by dehydrobromination of the corresponding aminotriphenylphosphonium bromides by sodamide in liquid ammonia (19,20) and were recrystallized from heptane.

N-substituted-Aminotriphenylphosphonium Bromides

The N-substituted-aminotriphenylphosphonium bromides were synthesized according to the procedures of Zimmer and Singh (19,20) and were recrystallized from chloroform-ethyl acetate.

Solvents

All solvents, reagent grade, were supplied from various commercial sources. They were used without purification except when dry solvents were required. Solvents were dried over sodium-benzophenone or phosphorus pentoxide and distilled under dry nitrogen.

Other Compounds

Sodamide, sodium hydride, and proton sponge were purchased from Aldrich Chemical Company and were used without further purification. Sodium dimethylaminoborohydride, as the dioxanate, was synthesized according to the procedure of Aftandilian et al. (49). The compound N,N-dimethylaminotriphenylphosphonium iodide was synthesized according to the procedure of Zimmer and Singh (19). Lithium borohydride was obtained from Metal Hydrides, Inc. and was recrystallized from diethylether. Tetra-n-butylammonium borohydride was purchased from Aldrich Chemical Company and was recrystallized from ethyl acetate (50). Trimethylamine iodoborane was synthesized according to the procedure of Ryschkewitsch and Wiggins (51) and was sublimed prior to use.

Procedures

Protection from the Atmosphere

All syntheses were performed in glassware which had been dried in an oven at 130° and that were cooled to room

temperature under a steady stream of dry nitrogen. All of the syntheses were performed either inside a dry box or in a hood maintaining a constant flow of dry nitrogen through the reaction flasks. Filtrations of water sensitive materials were done inside a dry box or by using standard Schlenk ware techniques.

Samples for nmr spectroscopy of water sensitive materials were prepared in a dry box, and the nmr tubes were sealed by a flame when solutions were to be kept for long periods of time.

Potassium bromide pellets for i.r. spectroscopy were prepared in a dry box using oven dried KBr. Infrared spectra were recorded under a stream of dry nitrogen.

All water sensitive materials were stored in dessicators and handled in a dry box.

Infrared Spectra

Infrared spectra were obtained on a Nicolet 5DXB FTIR spectrometer.

NMR Spectra

Proton and C^{13} nmr spectra were obtained at 99.55 and 25.00 MHz respectively on a JEOL FX-100 instrument with tetramethylsilane as internal reference. Occasionally, H^1 nmr spectra were obtained at 300 MHz on a Nicolet NT-300 instrument or at 60 MHz on a Varian EM360L when more or less resolution was appropriate. Phosphorus-31 nmr spectra were

obtained proton decoupled at 80.984 MHz or 121.477 MHz with 85% phosphoric acid as the external reference. Boron-11 nmr spectra were obtained at 64.184 MHz or 96.270 MHz with trimethylborate as the external reference. Methylene chloride, benzene, or monoglyme was used as the solvent. Deuterated solvents were used for the H^1 nmr spectra.

Mass Spectra

Mass spectra were obtained on an AEI-MS30 with an ionizing energy of 70 e.v.

Gas Chromatography

Gas chromatography was recorded on a Varian Model 3700 gas chromatograph using a 2.5 meter long 1/4 inch in diameter column packed with Porapak Q.

Calculations

All computer programs were performed on an Apple II computer.

Melting Point

Melting points of the various compounds were determined in sealed capillary tubes on a Thomas Hoover apparatus and were not corrected.

Constant Temperature

Temperatures were kept constant in a Haake FJ constant temperature bath.

Elemental Analyses

The elemental analyses were performed by Mr. Mel Courtney of the University of Florida.

CHAPTER III
SYNTHESES OF BORANE ADDUCTS AND BORON CATIONS

Syntheses of the N-alkyliminotriphenylphosphoranes and the β -N-substituted-aminoiminotriphenylphosphoranes, used in the borane adduct investigation, are represented by the preparation of a new phosphorane, β -N-phenylaminoimino-triphenylphosphorane. The apparatus consists of a nitrogen-flushed 500 ml three neck flask immersed in a dry ice acetone bath. The flask is fitted with a thimble, a dry ice condenser and a gas addition tube which is connected to an ammonia cylinder (see Figure 1).

To a suspension of β -N-phenylhydrazinotriphenylphosphonium bromide, 22.466 g (49.999 mmols), in 300 ml of anhydrous liquid ammonia, sodamide, 2.148 g (55.06 mmols), was added. The yellow mixture was stirred for one hour with a magnetic stirrer. The ammonia was then evaporated under a steady stream of dry nitrogen. The reaction flask was transferred to the dry box and 300 ml of dry tetrahydrofuran were added to the residue. The mixture was filtered leaving a white solid behind. The yellow-brown filtrate was evaporated under a steady stream of dry nitrogen to produce a yellow-brown solid which weighed 14.7896 g (80% yield).

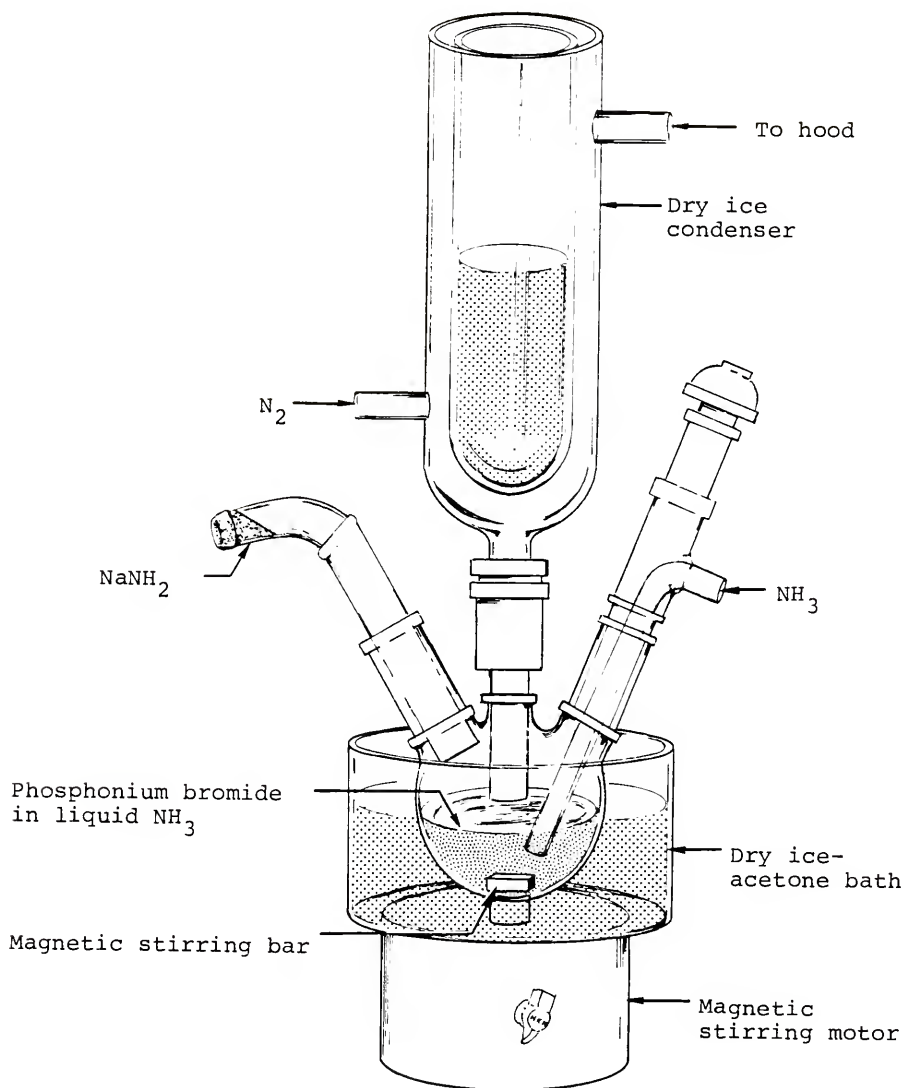
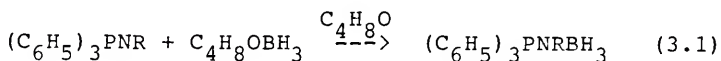


Figure 1. Apparatus for synthesis of phosphoranes.

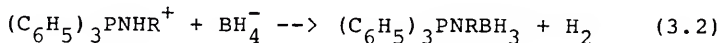
The crude product was recrystallized from a dry tetrahydrofuran-heptane solvent mixture to produce large yellow cubic crystals. The recovered material (9.7886 g, 66% yield) melted at 132-133°. The analysis of the recrystallized material was %C 78.05, %H 5.61, %N 7.41, calculated: %C 78.24, %H 5.75, %N 7.60.

Syntheses of Borane Adducts

Borane adducts of N-alkyliminotriphenylphosphoranes and β -N-substituted-aminoiminotriphenylphosphoranes were prepared by two simple synthetic methods. The first procedure employs displacement of a donor coordinated to BH_3 using borane-tetrahydrofuran complex and an N-substituted-iminotriphenylphosphorane (2,11).



The second procedure employs in situ generation of diborane in diethyl ether by reaction of lithium borohydride with a N-substituted-aminotriphenylphosphonium bromide.



Syntheses of N-Alkyliminotriphenylphosphorane Boranes
from Borane Tetrahydrofuran Complex and N-Alkylimino-
triphenylphosphoranes

In a typical experiment, twice the stoichiometric amount of borane-tetrahydrofuran complex was added via a syringe to a stirred saturated solution of a N-alkylimino-triphenylphosphorane in tetrahydrofuran. Using this procedure, N-alkyliminotriphenylphosphorane boranes were synthesized where alkyl = methyl, ethyl, n-propyl, isopropyl, isobutyl and tert-butyl. The general workup of this preparative method is represented by the synthesis of N-methyliminotriphenylphosphorane borane.

To N-methyliminotriphenylphosphorane, 1.381 g (4.740 mmoles), in 6 ml of dry tetrahydrofuran, borane-tetrahydrofuran complex, 8.00 ml of 1.00 molar (8.00 mmoles of BH_3), was added. The mixture was stirred for 1.5 hours with a magnetic stirrer. A white precipitate formed after 5 minutes of stirring. The product was further precipitated by the addition of 150 ml of dry heptane. The crude product was filtered and washed with four portions of 40 ml each of dry heptane (160 ml total). The solid was dried in vacuo. The product weighed 1.309 g (90% yield), mp 184-186° dec.

A portion of the crude product (0.269 g) was recrystallized from a dry benzene-heptane solvent mixture producing cubic crystals. The recovered material (0.170 g, 63%) melted at 190-191° with decomposition.

The yields of the N-alkyliminotriphenylphosphorane boranes and the melting points of the crude and recrystallized materials are given in Table 1. Analytical data for the N-alkyliminotriphenylphosphorane boranes are listed in Table 2.

Syntheses of β -N-Substituted-Aminoiminotriphenylphosphorane Boranes from Borane-Tetrahydrofuran Complex and β -N-Substituted-Aminoiminotriphenylphosphoranes

In a typical experiment, three times the stoichiometric amount of borane-tetrahydrofuran complex was added via a syringe to a stirred saturated solution of a β -N-substituted-aminoiminotriphenylphosphorane in tetrahydrofuran. Using this procedure, β -N-dimethyl, β -N-phenyl and β -N-methyl, phenylaminoiminotriphenylphosphorane boranes were synthesized. The general workup of this preparative method is represented by the synthesis of β -N-phenylaminoiminotriphenylphosphorane borane.

To β -N-phenylaminoiminotriphenylphosphorane, 1.8557 g (5.0370 mmols), in 35 ml of dry tetrahydrofuran, borane-tetrahydrofuran complex, 15.00 ml of 1.00 molar (15.0 mmols of BH_3), was added. The solution changed from dark yellow to a very light yellow upon addition of the borane tetrahydrofuran complex. The mixture was stirred for 2 hours with a magnetic stirrer. A yellowish precipitate

Table 1. Yields and Melting Points of N-Alkylimino- and β -N-Substituted-Aminoimino-Triphenylphosphorane Boranes.

Compounds	Yield of Borane %	Mp, C° of Crude Product	Mp, C° of Recrystallized Product
N-methyliminotriphenylphosphorane borane	90	184-186 dec	190-191 dec
N-ethyliminotriphenylphosphorane borane	92	176-180 dec	182-183 dec
N-n-propyliminotriphenylphosphorane borane	91	168-169 dec	169-170 dec
N-isopropyliminotriphenylphosphorane borane	90	171-176 dec	186-187 dec
N-isobutyliminotriphenylphosphorane borane	72	150-153 dec	158-159 dec
N-t-butyliminotriphenylphosphorane borane	94	183-187 dec	193-194 dec
β -N-dimethylaminoiminotriphenyl- phosphorane borane	83	125-126 dec	*
β -N-phenylaminoiminotriphenyl- phosphorane borane	72	126-127 dec	130-131 dec
β -N-methyl,phenylaminoimino- triphenylphosphorane borane	92	140-141 dec	141-142 dec

*The product obtained by precipitation from the reaction mixture was sufficiently pure to give a satisfactory elemental analysis.

Table 2. Analyses of N-Alkylimino- and β -N-Substituted-Aminoimino-Triphenylphosphorane Boranes.

Compounds		%C	%H	%N
$(C_6H_5)_3PNCH_3BH_3$	Calcd.	74.78	6.94	4.59
	Found	75.00	7.09	4.54
$(C_6H_5)_3PN(CH_2CH_3)BH_3$	Calcd.	75.26	7.26	4.39
	Found	75.15	7.31	4.26
$(C_6H_5)_3PN(n-C_3H_7)BH_3$	Calcd.	75.69	7.56	4.20
	Found	75.22	7.86	4.15
$(C_6H_5)_3PN(i-C_3H_7)BH_3$	Calcd.	75.69	7.56	4.20
	Found	75.63	7.68	4.10
$(C_6H_5)_3PN(i-C_4H_9)BH_3$	Calcd.	76.09	7.84	4.03
	Found	76.13	8.09	3.83
$(C_6H_5)_3PN(t-C_4H_9)BH_3$	Calcd.	76.09	7.84	4.03
	Found	76.02	8.04	3.91
$(C_6H_5)_3PNN(CH_3)_2BH_3$	Calcd.	71.88	7.24	8.38
	Found	71.63	7.38	8.10
$(C_6H_5)_3PNNH(C_6H_5)BH_3$	Calcd.	75.41	6.33	7.33
	Found	75.31	6.42	7.10
$(C_6H_5)_3PNNCH_3(C_6H_5)BH_3$	Calcd.	75.77	6.61	7.07
	Found	75.49	6.69	6.85

formed after 30 minutes of stirring. The product was further precipitated by the addition of 200 ml of dry heptane. The crude product was filtered and washed with four portions of 40 ml each of dry heptane (160 ml total). The solid was dried in vacuo. The product weighed 1.3802 g (72% yield), mp 126-127° dec.

A portion of the solid (0.8643 g) was dissolved in 75 ml of dry tetrahydrofuran. The solution was filtered, and dry heptane, 100 ml, was added slowly to the filtrate, with stirring, to precipitate fine white needles. The solid was filtered and washed with three portions of 50 ml each of dry heptane (150 ml total). The solid was dried in vacuo. The recovered material (0.6619 g, 77% yield) melted at 130-131° with decomposition.

The yields of the β -N-substituted-aminoiminotriphenylphosphorane boranes and the melting points of the crude and recrystallized materials are given in Table 1. Analytical data for the β -N-substituted-aminoiminotriphenylphosphorane boranes are listed in Table 2.

Syntheses of N-Substituted-Iminotriphenylphosphorane Boranes from Lithium Borohydride and N-Substituted-Aminotriphenylphosphonium Bromides

Two experiments were carried out to demonstrate the usefulness of this experimental method toward the two classes of compounds, the N-alkylaminotriphenylphosphonium bromides and the β -N-substituted-hydrazinotriphenylphosphonium bromides. The apparatus consists of a

nitrogen-flushed 100 ml three neck flask equipped with a pressure compensated addition funnel at A, a reflux condenser at B, and a nitrogen inlet tube at C, connected to a mercury bubbler (see Figure 2). The top of the reflux condenser is connected to a mercury bubbler.

Synthesis of N-methyliminotriphenylphosphorane borane.

To N-methylaminotriphenylphosphonium bromide, 1.893 g (5.085 mmoles), a solution of 0.147 g (6.75 mmoles), of lithium borohydride in 20 ml of dry diethyl ether was added via the funnel. The mixture was stirred for 1 hour with a magnetic stirrer during which time hydrogen gas evolution was observed. To the mixture was added 25 ml of dry diethyl ether. The funnel was removed and a stopper was placed at A. The inlet tube was moved from C and connected to the top of the reflux condenser, and a stopper was placed at C. The mixture was then heated to reflux for 4 hours. The flask was allowed to cool to room temperature, and the inlet tube was moved back to C. The top of the condenser was connected to a drying tube containing anhydrous calcium sulfate. The ether was then evaporated under a steady stream of dry nitrogen. The flask was transferred to a dry box. The residue in the flask was extracted with two portions of 80 ml each of dry benzene (160 ml total). The solutions were filtered, and the combined filtrate was evaporated under a steady stream of dry nitrogen. After evaporation, a yellowish white solid remained which weighed 0.916 g (59% yield).

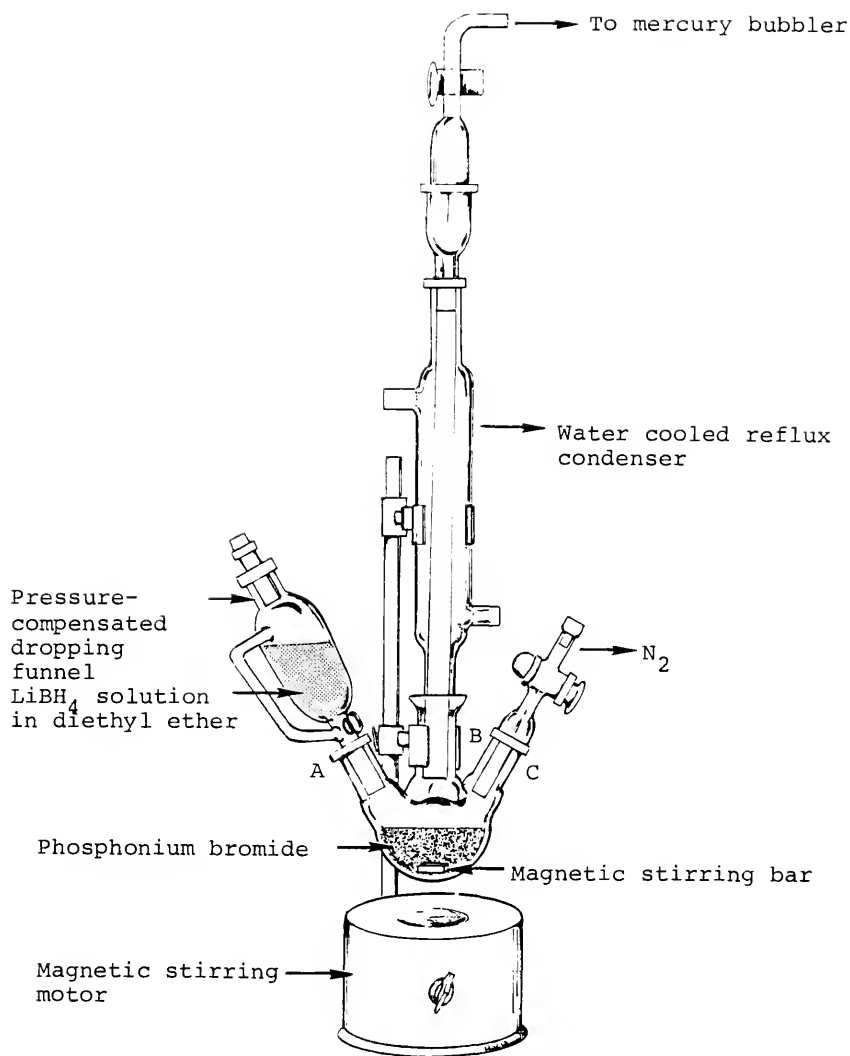


Figure 2. Apparatus for synthesis of borane adducts.

A portion of the solid (0.307 g) was recrystallized from a benzene-heptane solvent mixture producing 0.189 g (62% yield) of white cubic crystals. The melting point, H^1 and B^{11} nmr spectra of the product were identical to a previously prepared sample of N-methyliminotriphenylphosphorane borane.

Synthesis of β -N-Dimethylaminoiminotriphenylphosphorane Borane. To β -N-dimethylhydrazinotriphenylphosphonium bromide, 2.0200 g (5.0340 mmoles), a solution of 0.1591 g (7.304 mmoles) of lithium borohydride in dry diethyl ether was added via the funnel. The mixture was stirred for 2 hours with a magnetic stirrer, during which time hydrogen gas evolution was observed. To the mixture was added 60 ml of dry diethyl ether. The inlet tube was moved from C and connected to the top of the condenser, and a stopper was placed at C. The funnel was removed; a stopper was placed at A. The mixture was then heated to reflux for 4 hours. The flask was allowed to cool to room temperature and the inlet tube was moved back to C. The top of the reflux condenser was connected to a drying tube containing anhydrous calcium sulfate. The ether was then evaporated under a steady stream of dry nitrogen. The flask was transferred to a dry box. The residue in the flask was extracted with three portions of 50 ml each of dry benzene (150 ml total). The solutions were filtered and the combined filtrate was evaporated under a steady stream of

dry nitrogen. After evaporation, a white solid remained which weighed 1.417 g (84% yield).

A portion of the solid (1.1264 g) was dissolved in 25 ml of dry tetrahydrofuran. The solution was filtered. To the filtrate was added 150 ml of dry heptane to form a white precipitate. The precipitate was filtered and washed with four portions of 40 ml each of dry heptane (160 ml total). The solid was dried in vacuo and weighed 0.7422 g (66% yield). The melting point, H^1 and B^{11} nmr spectra of the solid were identical to a previously prepared sample of β -N-dimethylaminoiminotriphenylphosphorane borane.

A direct comparison of the two methods used to obtain borane adducts is given in Table 3. Materials used, yields, reaction times, and total time spent to isolate a crude product of N-methyliminotriphenylphosphorane borane are listed in Table 3.

Syntheses of Boron Cations

Boron cations of the type $(base)_2BH_2^+I^-$ where base = N-alkyliminotriphenylphosphorane were synthesized by displacement of iodide from an iodoborane prepared in situ (36). The iodoborane adducts were prepared by a modification of the method of Nöth and Beyer (52).

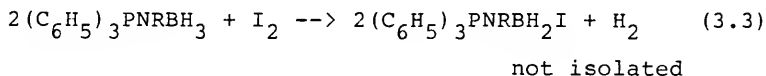
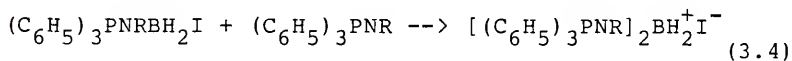


Table 3. Comparison of the Two Methods Used to Synthesize Borane Adducts.

	Method 1	Method 2
Materials used	THF ^a borane, THF, heptane, phosphorane	LiBH ₄ , diethyl ether, phosphonium bromide, benzene
Reaction time	1.5 hours	5 hours
Yield %	90	59
Total time	15 hours	24 hours

a = tetrahydrofuran.



In a typical experiment, a stoichiometric amount of iodine was added to a solution of the borane in benzene. After all the iodine had reacted, a stoichiometric amount of the corresponding phosphorane was added, and the reaction product was isolated. The reactions were run at room temperature. In this manner boron cations of the type bis(N-alkyliminotriphenylphosphorane)BH₂⁺I⁻, where

alkyl = methyl, ethyl and n-propyl, were synthesized. The general workup of this preparative method is represented by the synthesis of bis(N-methyliminotriphenylphosphorane) boronium iodide.

Synthesis of Bis(N-Methyliminotriphenylphosphorane)
Boronium Iodide

To N-methyliminotriphenylphosphorane borane, 0.341 g (1.12 mmoles), in 60 ml of dry benzene, iodine, 0.124 g (0.487 mmoles), was added. The solution was stirred with a magnetic stirrer. The iodine reacted rapidly evolving hydrogen gas. The iodine color disappeared after 10 minutes indicating that all of the iodine had reacted. To the yellowish cloudy solution, N-methyliminotriphenylphosphorane, 0.292 g (1.00 mmoles), was added. The mixture was stirred for 1.5 hours. A white precipitate was observed after 30 minutes of stirring. The precipitate was filtered and washed with five portions of 20 ml each of dry benzene (100 ml total). The solid was dried in vacuo. The product weighed 0.669 g (93% yield), mp 164-168°.

A portion of the crude product (0.282 g) was dissolved in a minimum amount of dry methylene chloride. The solution was filtered, and dry diethyl ether was added to the filtrate to precipitate 0.275 g of white powder (98% yield) mp 215-217°.

The yields of the bis(N-alkyliminotriphenylphosphorane) boronium iodides and the melting points of the crude and

reprecipitated products are given in Table 4. Analytical data for the boron cations are listed in Table 5.

Attempted Synthesis of (Trimethylamine) (N-n-Propyl-
iminotriphenylphosphorane) Boronium Iodide

To trimethylamine iodoborane, 1.0012 g (5.0352 mmoles), in 100 ml of dry benzene, N-n-propyliminotriphenylphosphorane, 1.6168 g (5.0622 mmoles), was added. The mixture was stirred for 14 hours with a magnetic stirrer. A white precipitate formed which was filtered and washed with five portions of 20 ml each of dry benzene (100 ml total). The solid was dried in vacuo. The product weighed 1.9025 g (73% yield).

A H^1 nmr spectrum of the solid in deuterated methylene chloride was recorded. The spectrum showed two sets of peaks. One set of peaks corresponded to bis(N-n-propyliminotriphenylphosphorane) boronium iodide, and the sharp singlet occurring at $\delta = 3.00$ ppm was identical with the chemical shift for bis(trimethylamine) boronium iodide in the same solvent. The ratio of the integrated areas under the peaks showed that an equimolar amount of both products was produced.

A portion of the solid (1.467 g) was added to 50 ml of deionized water. The solid was sparingly soluble, and the mixture was stirred for 10 minutes with a magnetic stirrer. The mixture was filtered, and the remaining solid was dried in vacuo. The recovered material weighed 1.202 g. A H^1 nmr

Table 4. Yields and Melting Points of Bis(N-Alkylimino-triphenylphosphorane) Boronium Iodides.

Compounds	Yield of Cation %	Mp, C° of Crude Product	Mp, C° of Recrystallized Product
Alkyl			
Methyl	93	164-168	215-217
Ethyl	73	186-190	197-199
n-Propyl	91	190-194	200-202

Table 5. Analyses of Bis(N-Alkyliminotriphenylphosphorane) Boronium Iodides.

Compounds		%C	%H	%N
[(C ₆ H ₅) ₃ PNCH ₃] ₂ BH ₂ ⁺ I ⁻	Calcd.	63.18	5.30	3.88
	Found	62.82	5.22	3.73
[(C ₆ H ₅) ₃ PN(C ₂ H ₅) ₂ BH ₂ ⁺ I ⁻	Calcd.	64.02	5.64	3.73
	Found	63.34	5.61	3.56
[(C ₆ H ₅) ₃ PN(n-C ₃ H ₇) ₂ BH ₂ ⁺ I ⁻	Calcd.	64.80	5.96	3.60
	Found	64.51	6.01	3.41

spectrum of the water insoluble material in deuterated methylene chloride was recorded. The spectrum showed two sets of peaks. One set of peaks corresponded to bis(N-n-propyliminotriphenylphosphorane) boronium iodide, and the other set corresponded to N-n-propylaminotriphenylphosphonium ion formed by the decomposition of the boron cation in water.

To the aqueous filtrate was added 30 ml of a saturated solution of ammonium hexafluorophosphate in deionized water. A white solid precipitated from the mixture. The precipitate was filtered and dried in vacuo. A H^1 nmr spectrum of the solid in methylene chloride was recorded. The spectrum showed only one peak, a singlet at $\delta = 2.50$ ppm. The peak corresponded to bis(trimethylamine) boronium hexafluorophosphate (29). The recovered weight, 0.370 g, corresponded to a 95% yield.

CHAPTER IV
PHYSICAL, CHEMICAL AND SPECTRAL PROPERTIES OF BORANE
ADDUCTS AND BORON CATIONS

Physical and Chemical Properties

Borane Adducts

General properties. The borane adducts of various N-substituted-iminotriphenylphosphoranes are white crystalline solids. They all have some solubility in methylene chloride, benzene, tetrahydrofuran and chloroform. Their solubility in various aliphatic hydrocarbons, namely heptane, is very poor. Therefore, heptane could be used as a precipitating agent. These compounds are also quite insoluble in water.

Thermal stability. In general, thermal stabilities of borane adducts vary according to which ligand group is attached to BH_3 . It has been reported (53) that trimethylamine borane can be heated for several hours at 125° without a detectable change in its physical properties. In contrast to trimethylamine borane, the pyridine boranes readily evolve hydrogen at temperatures below 100° to form red resins. Dimethylamine borane also evolves hydrogen at 200° to form dimethylamino borane (54,55). A few of the

borane adducts which have been made, namely carbonyl borane (2), dimethylether borane (3) and phosphine borane (5) are only stable at low temperatures and dissociate into the free bases and diborane below -20° .

The borane adducts prepared in this study are stable at room temperature. Samples stored for one year in closed containers gave no noticeable change in appearance or in their H^1 nmr spectra. The adducts are unstable at elevated temperatures, and all of the boranes decompose at their melting points evolving hydrogen. The mode of decomposition is represented by the pyrolysis of N-n-propyliminotriphenylphosphorane borane.

A sample of N-n-propyliminotriphenylphosphorane borane was heated to 190° for 20 minutes under an atmosphere of dry argon. Hydrogen evolution was observed at the melting point. A H^1 nmr spectrum of the recovered material in deuterated benzene gave a complex spectrum with several new overlapping peaks in the 0-3 ppm region. A P^{31} nmr spectrum of the same material showed only two resonances: a major peak corresponding to triphenylphosphine and a very minor peak corresponding to triphenylphosphine borane. A B^{11} nmr spectrum, proton decoupled, gave a peak corresponding to triphenylphosphine borane and two broad humps in the region 0 to -30 ppm indicating sp^2 bonded borons (56).

Hydrolytic stability. The stabilities of borane adducts toward hydrolysis also depend upon which group is coordinated to BH_3 . Phosphine borane (5) and borane

tetrahydrofuran complex react rapidly with water to form hydrogen and boric acid. Reports indicate that pyridine borane (57) and substituted pyridine boranes (58) react only slowly with water. The kinetics of hydrolysis of trimethylamine borane have been studied in detail by Ryschkewitsch (59) and demonstrate that the reaction with water is quite slow. Heal (60) reports that triphenylphosphine borane is unaffected by moist air, water, 2N sodium hydroxide and 6N hydrochloric acid solutions.

The borane adducts prepared in the current investigation are not stable towards hydrolysis, but react slowly with water. Samples could be handled in a humid atmosphere for short periods of time without evidence of decomposition. A crystalline sample of N-methyliminotriphenylphosphorane borane was allowed to sit out in a moist atmosphere for two days. Examination of the crystals under a microscope showed pitting of the surface indicating that some decomposition had occurred.

Boron Cations

General properties. The boron cations of the type bis(N-alkyliminotriphenylphosphorane) boronium iodide are white solids. The iodide salts are very soluble in methylene chloride and chloroform but are insoluble in benzene, water, diethyl ether, heptane and tetrahydrofuran. Their insolubility in benzene and diethyl ether made these solvents ideal precipitating agents.

Thermal stability. The boronium iodides prepared in this study are stable indefinitely at room temperature when stored under a dry nitrogen atmosphere. The P^{31} nmr spectra of these compounds, taken after 1 year, did not show any change. On heating in sealed capillary tubes, the salts changed color at their melting points. The change in the color of the molten salt was irreversible on cooling, probably due to decomposition.

Hydrolytic stability. Boron cations exhibit varying stabilities toward hydrolysis. For example, the stability increases with the base strength of the donor attached to boron. Salts of the bisamine cations show remarkable stability and have been recovered without change from concentrated acids and from 10% sodium hydroxide, even when heated to 100° for prolonged periods (32). On the other hand, cations containing tertiary phosphorus as a donor are stable toward acid and neutral solutions but are decomposed by hot aqueous base. Boron cations containing substituted pyridines as donor groups have been reported to be slowly attacked by boiling neutral and basic solutions (37). Cations containing dialkyl sulfides are decomposed rapidly in cold water. These observations show that generally, acid in low concentrations retards decomposition while base accelerates the reaction.

The boron cations prepared in this study are not stable toward acid and neutral solutions but appear to be stable in cold aqueous base for short periods of time.

In order to obtain detailed information regarding the hydrolytic stability of the boron cations, the following experiment was performed employing bis(N-n-propylimino-triphenylphosphorane) boronium iodide as representative of the group.

Three flasks were numbered and charged with the following materials:

Flask 1. 0.6270 g (0.8056 mmol) of
 $[(C_6H_5)_3PN(n-C_3H_7)]_2BH_2^+I^-$ + 50 ml
 of 1 M HCl.

Flask 2. 0.4761 g (0.6117 mmol) of
 $[(C_6H_5)_3PN(n-C_3H_7)]_2BH_2^+I^-$ + 50 ml
 of H_2O .

Flask 3. 0.4531 g (0.5822 mmol) of
 $[(C_6H_5)_3PN(n-C_3H_7)]_2BH_2^+I^-$ + 50 ml
 of 1 M NaOH.

The mixtures were vigorously stirred for 15 minutes and then rapidly filtered. The solids were dried in vacuo over P_2O_5 . Proton and P^{31} nmr spectra of the recovered materials were recorded in deuterated methylene chloride, and the following results were obtained:

- (1) The H^1 nmr spectrum showed only peaks in the phenyl region. The P^{31} nmr spectrum showed only

one peak corresponding to triphenylphosphine oxide in the same solvent.

- (2) The H^1 nmr spectrum showed two sets of peaks corresponding to unreacted boron cation and to N-n-propylaminotriphenylphosphonium ion. The P^{31} nmr spectrum showed two peaks corresponding to the same materials identified in the H^1 spectrum. The integrated areas of the peaks in the P^{31} spectrum showed that the ratio of boron cation to phosphonium ion was 3:1.
- (3) The H^1 nmr spectrum showed one set of peaks corresponding to unreacted boron cation. The P^{31} nmr spectrum showed only one peak also corresponding to unreacted boron cation.

In conclusion, the boron cation was completely decomposed by cold 1 M HCl, partially decomposed by neutral water and was recovered unreacted from 1 M NaOH. The triphenylphosphine oxide recovered from reaction 1 weighed 0.369 g (82% yield). This product is not an unexpected one, since some iminotriphenylphosphoranes are known to be decomposed by water to the corresponding amines and triphenylphosphine oxide (19,20,22,23,41). The above observations are surprising in that they contrast boron cation stability data reported in the literature. The observations indicate that

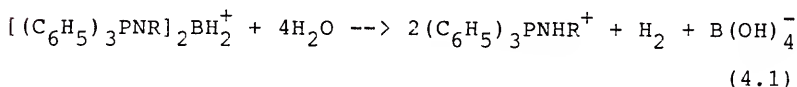
the mode of decomposition of the cations must be different than in bis(amine) boronium ions. The observation that hot aqueous acid does not attack bis-amine boron cations indicates that either the hydrogens on the boron are shielded by the bulky amine groups or that the hydridic character is reduced by the positive charge on the molecule (61).

Separate experiments show the N-alkylaminotriphenylphosphonium ions to be stable in cold aqueous neutral and acidic solutions for short periods of time. Therefore, the different reaction products from the acidic and neutral solutions described before indicate that two different mechanisms must occur both following initial attack of the hydridic hydrogens by acidic protons.

Attack of a hydridic hydrogen by a hydronium ion would produce hydrogen gas and a dication having water bound to the boron. The oxygen bound protons would be expected to be quite acidic because of the positive formal charge on the oxygen.

In the neutral solution, the hydronium ions would come from the autoionization of water. Thus, for every hydronium ion that reacted, a hydroxide ion must be produced. The hydroxide ion would be expected to abstract an acidic proton from the dication to produce a mono cation containing a B-O-H group. A lone pair on the oxygen could then donate electrons to the boron and cause the coordinated phosphorane to leave. The resulting boron fragment would most likely be coordinated by water and contain a single positive charge.

The free base would react with the water to form the corresponding phosphonium ion and hydroxide ion. The hydroxide ion would be expected to attack the boron cation, removing the acidic proton. Thus, hydroxide ion would not be expected to attack the phosphonium ion in neutral solution to produce triphenylphosphine oxide. The net equation for decomposition in neutral solution is as follows:



In the acidic solution, the hydroxide ion concentration would be negligible. Therefore, the coordinated phosphorane would not be expected to free itself from the dication. The high positive charge on the ion would be expected to activate the phosphorus toward attack by water through delocalization of charge by resonance. Thus, attack of phosphorus by water would produce the observed product, triphenylphosphine oxide.

Stability towards oxidizing agents. To a solution of bis(N-ethyliminotriphenylphosphorane) boronium iodide in dry methylene chloride, silver hexafluorophosphate was added. Rapid hydrogen evolution was observed immediately. A black solid remained which was filtered and then dissolved in 15 M nitric acid with evolution of NO_2 . The resulting solution was mixed with a solution of HCl to precipitate white silver

chloride. This result contrasts reports (37,61) on the properties of bis(amine) boronium ions which are unaffected by Ag(I) ion. Therefore, our boron cations possess substantial hydridic character.

Stability towards borohydride ion. In general, solutions of the three bis(N-alkyliminotriphenylphosphorane) boronium iodides were treated with stoichiometric amounts of tetra-n-butyl-ammonium borohydride. The following experiment is representative of the group.

To N-methyliminotriphenylphosphorane borane, 0.4560 g (1.494 mmol), in 25 ml of dry methylene chloride, iodine, 0.1884 g (0.7423 mmol), was added. The solution was stirred with a magnetic stirrer. Rapid hydrogen evolution was observed, and the iodine color disappeared after 10 minutes indicating that all of the iodine had reacted. To the solution, N-methyliminotriphenylphosphorane, 0.4298 g (1.475 mmol), was added. The solution was stirred for 1 hour under an inert atmosphere of dry nitrogen.

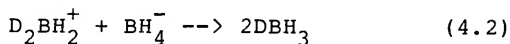
Approximately one half of a milliliter of the solution was transferred to a nmr tube. Phosphorus-31 and B¹¹ nmr spectra were recorded proton decoupled, and both showed only one peak corresponding to bis(N-methyliminotriphenylphosphorane) boronium iodide.

To the solution, tetra-n-butyl-ammonium borohydride, 0.3750 g (1.457 mmol), was added. The solution was stirred for seven days under an inert atmosphere of dry nitrogen. After three hours of stirring, approximately

one half of a milliliter of the solution was transferred to a nmr tube. A B^{11} nmr spectrum was recorded proton decoupled and showed only two peaks corresponding to the boron cation and to borohydride ion. A P^{31} nmr spectrum was recorded and showed only one peak corresponding to the boron cation.

The reaction was monitored periodically over the 7 day reaction time via B^{11} and P^{31} nmr. The spectra showed that the boron cation and borohydride ion reacted slowly to form the corresponding borane adduct exclusively. The final spectra obtained after 7 days showed only one peak each corresponding to the borane adduct.

In conclusion, all the boron cations reacted slowly with borohydride ion to form the corresponding borane adducts. The results show that the borane adducts are more stable thermodynamically than mixtures of the boron cations and borohydride ion. Although no specific kinetic studies were done, the sluggishness of the reactions between the boron cations and borohydride ion indicates that the transition state must be a high energy situation. The general equation for the transformation is as follows:



Spectral Properties

The Infrared Spectra of Phosphoranes, Borane Adducts and Boron Cations

The infrared spectra were obtained in KBr pellets using the Nicolet 5DXB FTIR spectrometer.

All of the phosphoranes, borane adducts and boron cations exhibit complex infrared spectra. In each spectrum, characteristic peaks corresponding to P-C, C-N and P=N stretching frequencies were assigned.

In general, the vibrational frequencies of the P-C groups are sharp and of moderate intensity. In all cases the P-C stretching frequencies are between 1432 and 1442 cm^{-1} . The observed peaks are in good agreement with observations made by Daasch and Smith (62). They examined the infrared spectra of a considerable series of aryl phosphorus compounds containing the P-aryl group.

The vibrational frequencies of the C-N groups are not as sharp as the P-C peaks and vary in intensity from very intense to moderately intense. Two different sets of C-N peaks were identified corresponding to aliphatic and aromatic groups attached to nitrogen. In general, the vibrational frequencies of the aliphatic C-N groups lie in the region between 1105 and 1117 cm^{-1} . The vibrational frequencies of the aromatic C-N groups lie in the region between 1302 and 1312 cm^{-1} . The observed C-N stretching frequencies are in good agreement with the correlations made by Colthup (63) for aromatic and aliphatic amines.

It was observed in the current study that by progressing through a series of free base to borane adduct to boron cation that the P-C and C-N stretching frequencies do not change to any significant extent.

In general, the vibrational frequencies of the P=N groups are broad and vary in intensity from very intense to weak. The stretching frequencies of the P=N group were assigned by straightforward comparisons between the spectra of the boronium cations, borane adducts and the uncoordinated phosphoranes. The assignments were made by finding peaks which changed to a significant extent along the series of free base to borane adduct to boron cation. This corresponds to the reasoning that by adding a BH_3 unit, the increase in mass and decrease in $d_{\pi-\text{p}_{\pi}}$ bonding should cause a shift to lower wavenumbers. The assigned frequencies for P-N stretching are in the broad region between 879 and 1335 cm^{-1} .

Several workers have attempted to identify a characteristic P=N stretching frequency. Horner and Oediger (21) made assignments in a series of N-(substituted phenyl)-iminotriphenylphosphoranes for the P=N stretches between 1160 and 1180 cm^{-1} . Allcock (64) presents an excellent discussion of P=N vibrational assignments. The collective data presented in his discussion show that, in cyclic structures, the absorptions are found at higher frequencies in the 1200 to 1400 cm^{-1} region. The data also show that

many mono-iminophosphoranes have a characteristic P=N stretching vibration in the 1325 to 1375 cm^{-1} region.

By attaching BH_3 units to the N-alkyliminotriphenylphosphoranes, a shift toward lower wavenumbers of between 31 to 105 cm^{-1} in the P=N stretching frequency is seen. By attaching BH_3 units to the β -N-substituted-aminoimino-triphenylphosphoranes, a smaller shift toward lower wavenumbers of between 0 to 27 cm^{-1} is seen. When comparing borane adducts to the corresponding boron cations, a shift on the order of 7 to 15 cm^{-1} in the P=N vibrational frequencies is evident, and the direction is random.

Presumably, there is a rough correlation between increasing coordinate π character and increasing vibrational frequency for P=N vibrations. Any correlation for the P=N link, however, must be expected to be mass sensitive and therefore liable to considerable frequency shifts with minor alterations in structure. This correlation is also only valid if the P=N vibrations do not participate in combination vibrations with the groups attached to phosphorus or nitrogen. The correlation is not, therefore, a particularly useful one in interpreting small frequency differences.

Two B-H stretching vibrations, symmetrical and antisymmetrical, are expected for a BH_3 group. In addition to these, two B-H deformation modes, bending and wagging, are also expected. In general, the asymmetrical stretch will occur at a higher frequency than the symmetric stretch, and the bending mode will occur at a higher frequency than the

wagging mode. Also, the stretching vibrations will occur at much higher frequencies than the deformations. In general, the vibration frequencies of the BH_3 groups of the borane adducts in this study are similar to the infrared data reported in the literature (65,66).

Symmetrical and antisymmetrical stretching vibrations are also expected for a BH_2 grouping as well as a symmetrical deformation vibration. The B-H stretching frequencies appeared in the region between 2274 and 2329 cm^{-1} and the deformation vibrations appeared in the region between 1185 and 1210 cm^{-1} (32,37). Compared to the borane adducts, the B-H stretching and deformation frequencies of our boron cations occur at higher wavenumbers, but at lower wavenumbers than in bis-amine cations (29).

The B-N stretches in the borane adducts and boron cations appeared in the region between 882 and 936 cm^{-1} . The B-N stretching frequencies of the cations were not much different from the corresponding borane adducts.

All of the assignments for the B-H and B-N modes were made by straightforward comparisons between the spectra of the borane and boronium complexes and the spectra of the uncoordinated phosphoranes.

Various infrared assignments are given in Tables 6, 7 and 8. Spectra of N-ethyliminotriphenylphosphorane and β -N-dimethylaminoiminotriphenylphosphorane are reproduced in Figures 3 and 4 respectively as examples for infrared

Table 6. Infrared Data of N-Alkylimino- and β -N-Substituted-Aminoimino-Triphenylphosphoranes.

Compounds	P-C Stretch cm^{-1}	P-N Stretch 879-1335 cm^{-1} broad	C-N Stretch 1105-1311 cm^{-1}
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{CH}_3)$	1435	1230	1108
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{C}_2\text{H}_5)$	1434	1228	1106
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{n-C}_3\text{H}_7)$	1432	1204	1106
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{i-C}_3\text{H}_7)$	1434	1335	1105
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{i-C}_4\text{H}_9)$	1434	1224	1107
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{t-C}_4\text{H}_9)$	1440	1281	1106
$(\text{C}_6\text{H}_5)_3\text{PNN}(\text{CH}_3)_2$	1434 ^a 1440 ^a	941	1114 1107 ^a
$(\text{C}_6\text{H}_5)_3\text{PNNH}(\text{C}_6\text{H}_5)^b$	1437	908	1305
$(\text{C}_6\text{H}_5)_3\text{PNN}(\text{CH}_3)(\text{C}_6\text{H}_5)$	1436	879	1311 ^c 1117 ^d

^adoublet; ^bthe NH stretching frequency is 3186 cm^{-1} ;
^caromatic; ^daliphatic.

Table 7. Infrared Data of N-Alkylimino- and β -N-Substituted-Aminoimino-Triphenylphosphorane Boranes.

Compounds	P-C Stretch cm	P-N Stretch 879-1179 cm	C-N Stretch 1105-1312 cm	Asymmetric Symmetric B-H Stretch cm	Bending Wagging RH ₃ Deformations cm	B-N Stretch
(C ₆ H ₅) ₃ PN(CH ₃)BH ₃	1437	1171	1114	2262 2232	1122 1072	889
(C ₆ H ₅) ₃ PN(C ₂ H ₅)BH ₃	1438	1173	1111	2264 2237	1126 1078	900
(C ₆ H ₅) ₃ PN(n-C ₃ H ₇)BH ₃	1436	1173	1109	2275 2240	1136 1085	900
(C ₆ H ₅) ₃ PN(i-C ₃ H ₇)BH ₃	1440	1142	1109	2275 2246	1130 1071	893
(C ₆ H ₅) ₃ PN(i-C ₄ H ₉)BH ₃	1438	1179	1113	2272 2239	1140 1072	882
(C ₆ H ₅) ₃ PN(t-C ₄ H ₉)BH ₃	1442	1176	1105	2275 2242	1138 1076	898
(C ₆ H ₅) ₃ PNN(CH ₃) ₂ BH ₃	1438	918	1114	2302 2237	1162 1090	931

Continued

Table 7. Continued.

Compounds	P-C Stretch cm ⁻¹	P-N Stretch 879-1179 cm ⁻¹	C-N Stretch 1105-1312 cm ⁻¹	Asymmetric Symmetric B-H Stretch cm ⁻¹	Bending Wagging BH ₃ Deformations cm ⁻¹	B-N Stretch cm ⁻¹
(C ₆ H ₅) ₃ PNNH(C ₆ H ₅)BH ₃ ^a	1438	881	1302	2287 2233	1133 1076	892
(C ₆ H ₅) ₃ PNN(CH ₃)(C ₆ H ₅)BH ₃	1437	879	1312 ^b 1114 ^c	2284 2245	1164 1085	936

^aThe N-H stretching frequency is 3260 cm⁻¹; ^baromatic; ^caliphatic.

Table 8. Infrared Data of Bis-(N-Alkyliminotriphenylphosphorane) Boronium Iodides.

Compounds	P-C Stretch cm ⁻¹	P-N Stretch cm ⁻¹ Broad	C-N Stretch cm ⁻¹	Asymmetric Symmetric		
				B-H Stretch cm ⁻¹	BH ₂ Deformation	B-N Stretch
$[(C_6H_5)_3PN(CH_3)]_2BH_2I^+$	1438	1164	1109	2329 2281	1185	916
$[(C_6H_5)_3PN(C_2H_5)]_2BH_2I^+$	1437	1185	1110	2323 2275	1210 ^a	899
$[(C_6H_5)_3PN(n-C_3H_7)]_2BH_2I^+$	1437	1187	1109	2321 2274	1210 ^a	896

^aOverlaps with P-N stretch.

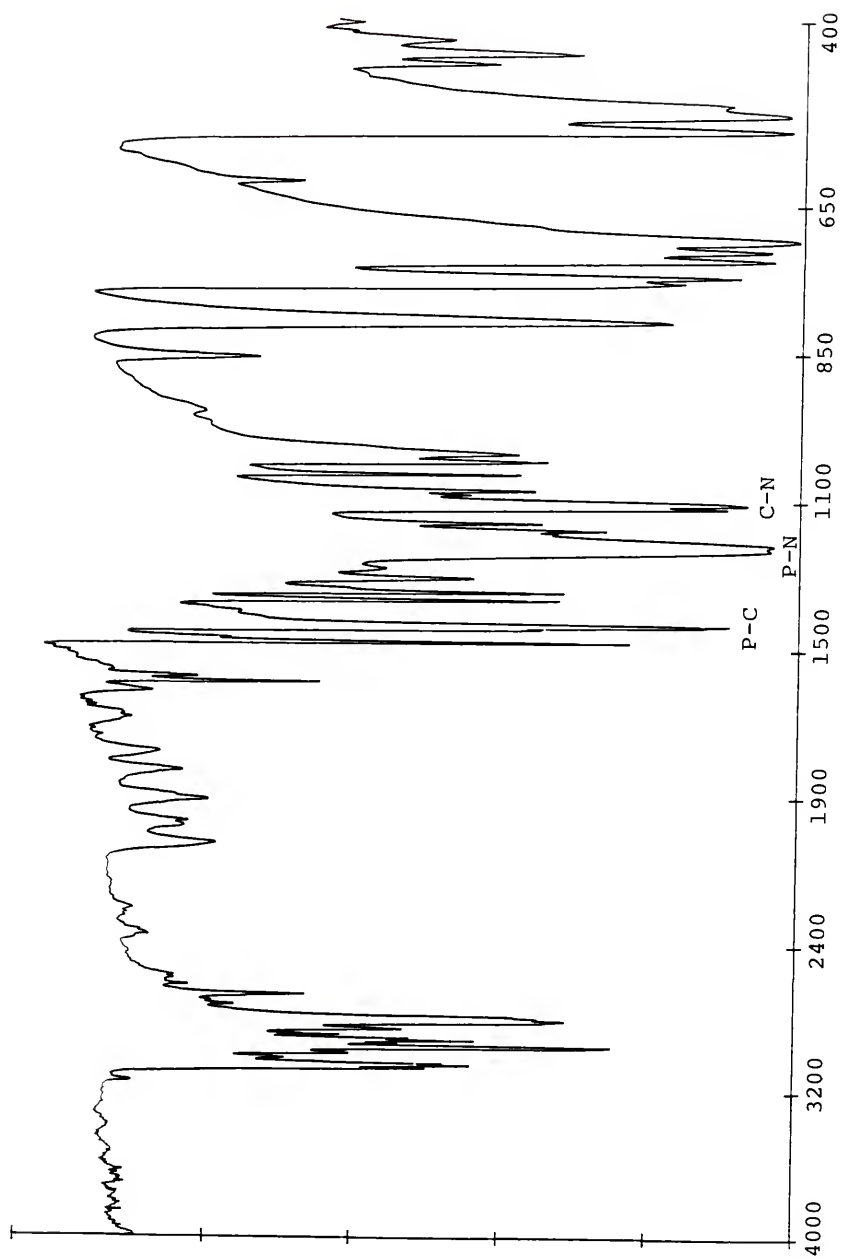


Figure 3. Infrared spectrum of N-ethyliminotriphenylphosphorane.

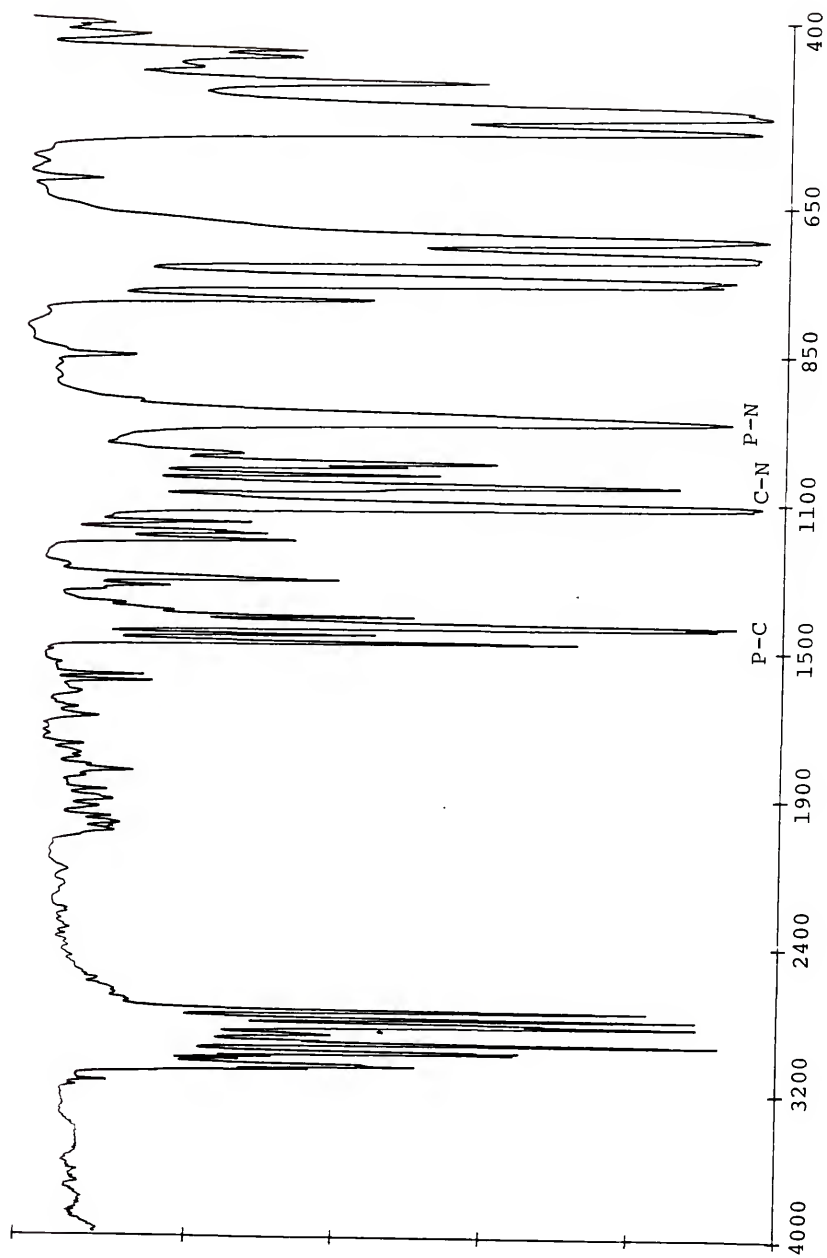


Figure 4. Infrared spectrum of β -N-dimethylaminoiminotriphenylphosphorane.

spectra of phosphoranes. Spectra of N-tert-butylimino-triphenylphosphorane borane and β -N-phenylaminoimino-triphenylphosphorane borane are reproduced in Figures 5 and 6 respectively as examples for infrared spectra of borane adducts. The spectrum of bis(N-methyliminotriphenylphosphorane) boronium iodide is reproduced in Figure 7 as an example for infrared spectra of boronium iodides.

The Mass Spectrum of N-Ethyliminotriphenylphosphorane Borane

The mass spectrum was obtained on an AEI-MS30 instrument employing an ionizing energy of 70 e.v. The spectrum was recorded using a crystalline sample. The mass spectrum is quite complex, and more than one fragmentation pattern appears. The parent ion peak is found at 319. Two different fragmentation patterns can be postulated which are consistent with the mass spectral data. In the first, the molecular ion loses hydrogen stepwise to form the fragment located at 316 corresponding to $(C_6H_5)_3PN(C_2H_5)B^+$. This fragment then loses boron to form the fragment $(C_6H_5)_3PN(C_2H_5)^+$ located at 305. Loss of a methyl group from this fragment forms the fragment $(C_6H_5)_3PNCH_2^+$ found at 290. The fragment at 290 then loses NCH_2 to form $(C_6H_5)_3P^+$ located at 262. The second fragmentation pattern is much simpler than the first. The molecular ion loses an ethyl group to form $(C_6H_5)_3PNBH_3^+$ found at 290. This fragment then loses NBH_3 to form $(C_6H_5)_3P^+$. The rest of the fragmentation

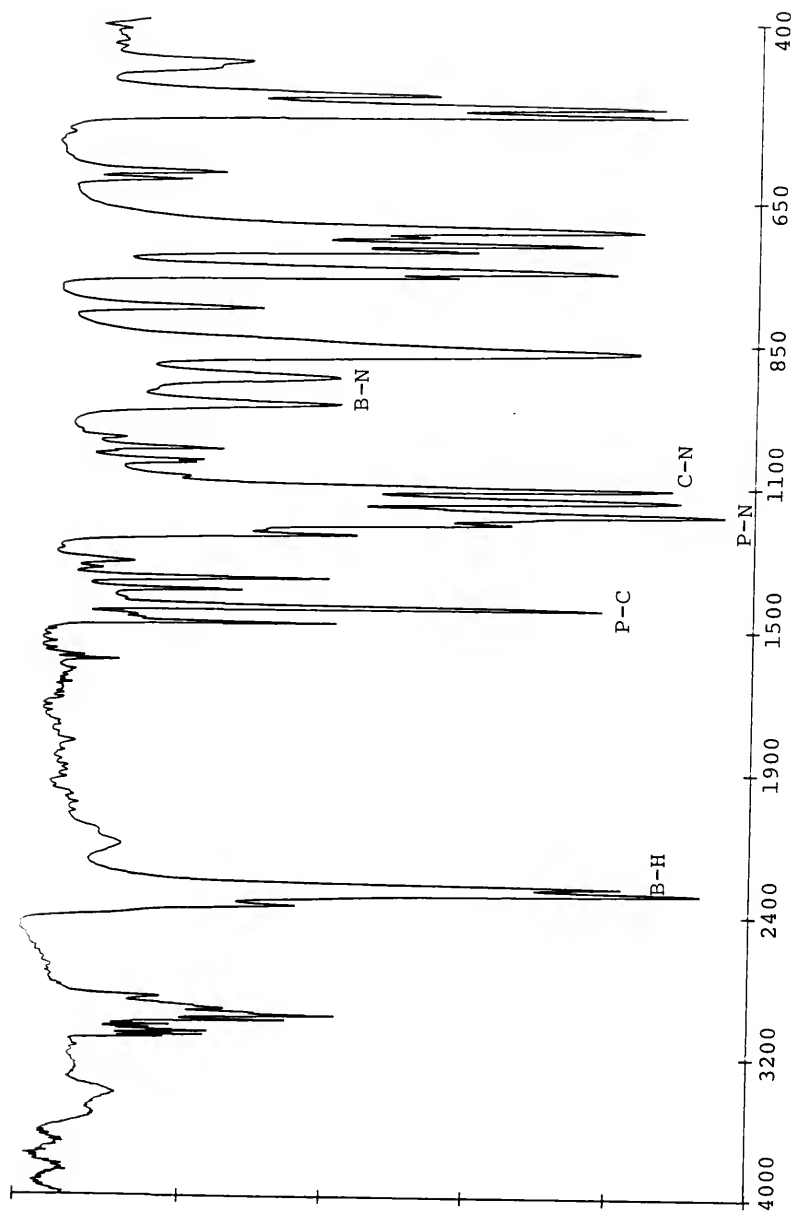


Figure 5. Infrared spectrum of N-tert-butyliminotriphenylphosphorane borane.

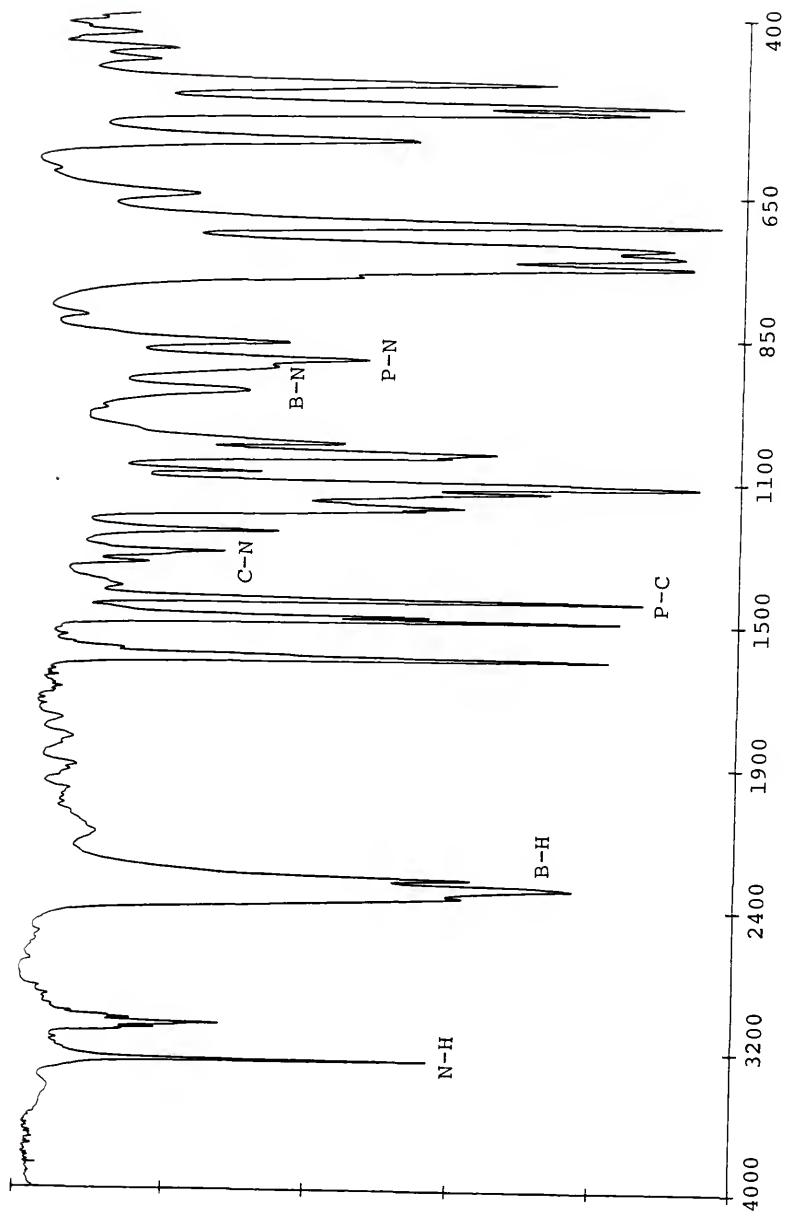


Figure 6. Infrared spectrum of β -N-phenylaminoiminotriphenylphosphorane borane.

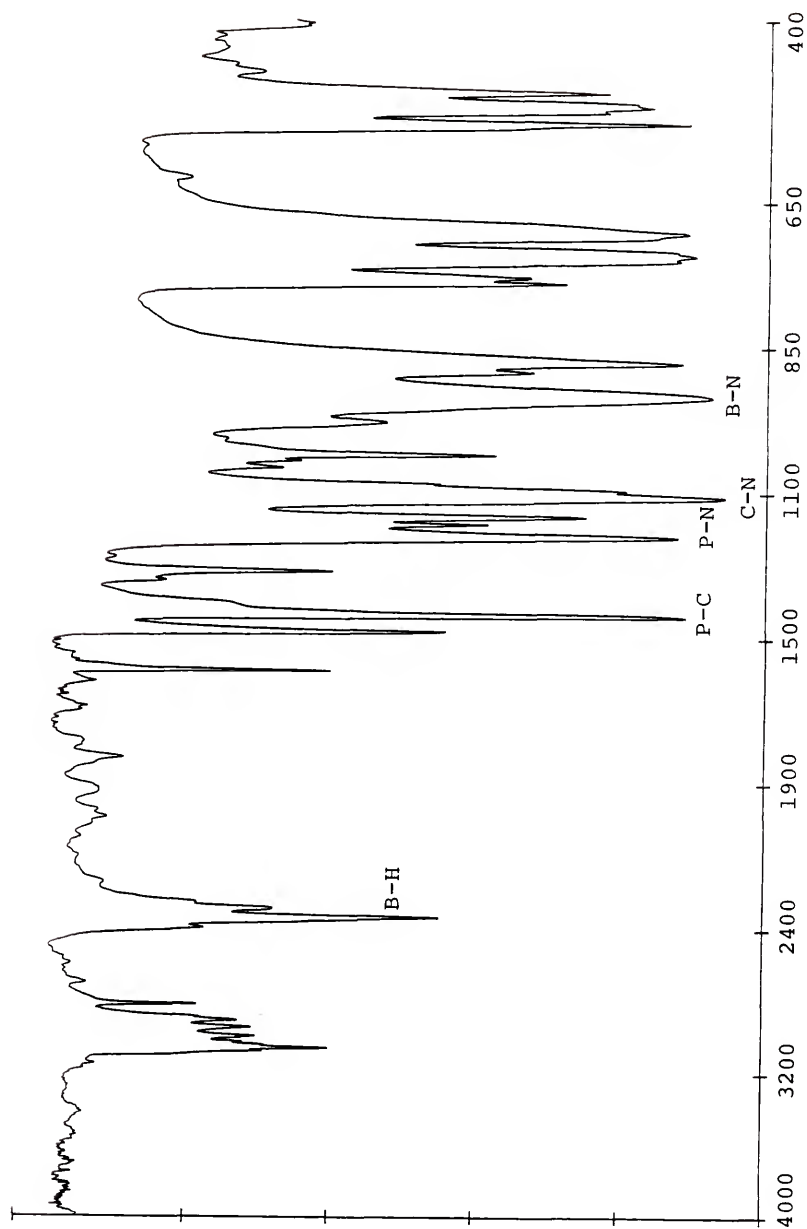
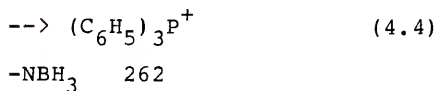
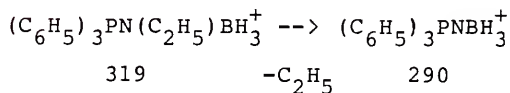
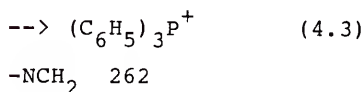
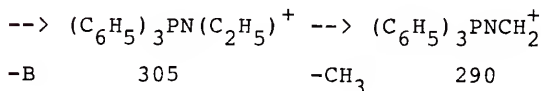
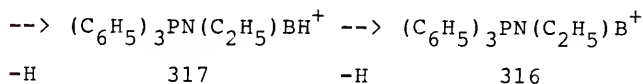
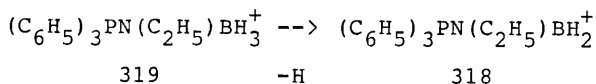


Figure 7. Infrared spectrum of bis-(N-methyliminotriphenylphosphorane) boron iodide.

pattern is almost identical to the mass spectrum of tri-phenylphosphine (67). The peaks at 28 and 18 correspond to nitrogen and water respectively from the atmosphere. The two fragmentation patterns are represented by the following equations:



The second fragmentation pattern is similar to the fragmentation pattern of trimethylamine borane (68).

Trimethylamine borane loses a methyl radical to form a very stable fragment corresponding to $(\text{CH}_3)_2\text{NBH}_3^+$ at 58. The mass spectrum of N-ethyliminotriphenylphosphorane borane is reproduced in Figure 8 and the intensity results are presented in Table 9.

Nuclear Magnetic Resonance Spectra

Proton nmr spectra of the phosphoranes, borane adducts and boron cations were taken on the JEOL FX-100 instrument with tetramethylsilane as an internal reference. The compounds N-n-propyliminotriphenylphosphorane borane and N-isobutyliminotriphenylphosphorane borane required higher resolution to determine their coupling patterns. Consequently, the H^1 nmr spectra of these two materials were taken on the Nicolet NT-300 instrument. Phosphorus-31 spectra were obtained proton decoupled at 80.984 MHz or 121.477 MHz with 85% phosphoric acid as the external reference. Boron-11 spectra were taken at 64.184 MHz or 96.270 MHz with trimethylborate as the external reference. Shifts for the P^{31} and B^{11} spectra are reported with negative ppm downfield from the corresponding references. Deuterated methylene chloride was used as the solvent for the H^1 and B^{11} spectra. Benzene was used as the solvent for the P^{31} spectra except in the case of the boron cations in which methylene chloride was used. The chemical shifts, δ , in parts per million and coupling constants, J, in hertz, of H^1 resonances plus the chemical shifts, δ , in parts per

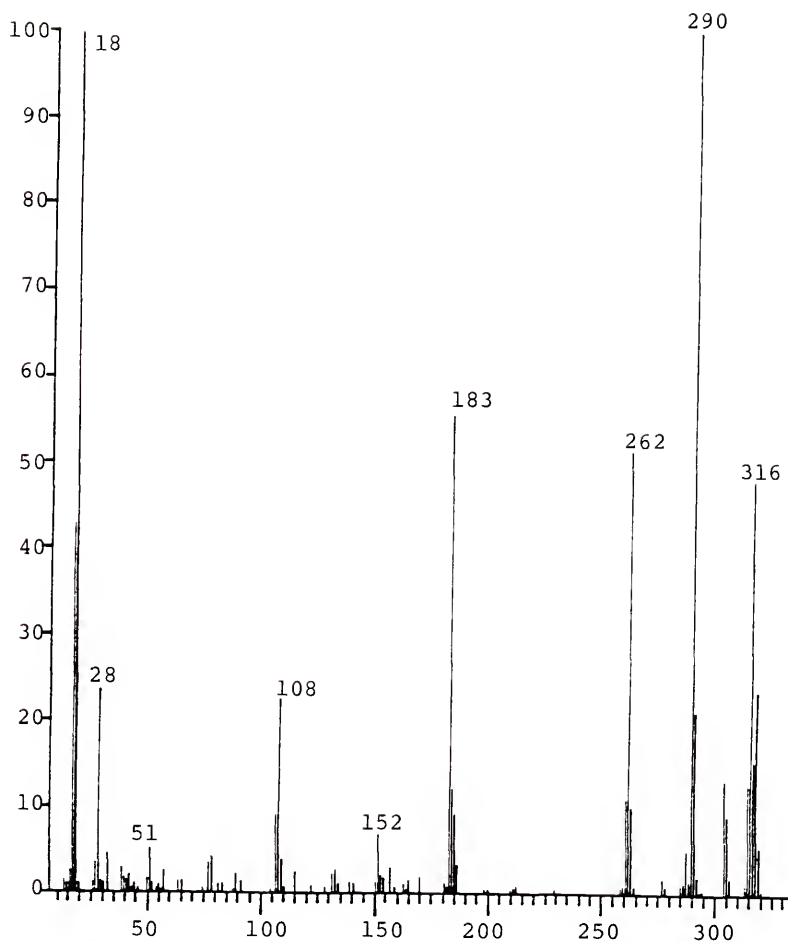


Figure 8. Mass spectrum of N-ethyliminotriphenylphosphorane borane.

Table 9. Mass Intensity Data for N-Ethyliminotriphenylphosphorane Borane.

Mass	Absolute Intensity	% Intensity of 290
320	231	0.53
319	2403	5.54
318	10230	23.60
317	6792	15.67
316	20889	48.20
315	145	0.33
315	5387	12.43
314	447	1.03
306	817	1.89
305	3928	9.06
304	5778	13.33
294	229	0.53
293	184	0.42
292	918	2.12
291	9265	21.38
290	43341	100.00
289	664	1.53
288	2213	5.11
287	546	1.26
286	505	1.17
278	401	0.93
277	804	1.86
276	712	1.64
264	379	0.87
263	4396	10.14
262	22343	51.55
261	4812	11.10
260	442	1.02
259	314	0.72

Continued

Table 9. Continued.

Mass	Absolute Intensity	% Intensity of 290
229	198	0.46
212	418	0.96
211	266	0.61
210	200	0.46
200	178	0.41
198	256	0.59
186	1434	3.31
185	3989	9.20
184	5286	12.20
183	24079	55.56
182	314	0.72
181	490	1.13
170	788	1.82
165	634	1.46
164	160	0.37
163	372	0.86
159	251	0.58
157	1245	2.87
154	698	1.61
153	863	1.99
152.5	397	0.92
152	2954	6.82
151	501	1.16
141	407	0.94
139	493	1.14
134	420	0.97
133	1074	2.48
131	895	2.07
128	241	0.56
122	269	0.62

Continued

Table 9. Continued.

Mass	Absolute Intensity	% Intensity of 290
115	1005	2.32
110	236	0.54
109	1530	3.53
108	9703	22.39
107	3894	8.98
104	130	0.30
91	515	1.19
89	906	2.09
88	170	0.39
83	420	0.97
81	380	0.88
78	1761	4.06
77	1510	3.48
74	200	0.46
65	508	1.17
63	496	1.14
57	293	0.68
57	755	1.74
56	174	0.40
55	394	0.91
54	234	0.54
52	515	1.19
51	2214	5.11
50	745	1.72
46	162	0.37
44	474	1.09
43	227	0.52
42	908	2.10
41	670	1.55
40	712	1.64

Continued

Table 9. Continued.

Mass	Absolute Intensity	% Intensity of 290
39	1222	2.82
32	1912	4.41
30	427	0.99
29	644	1.49
28	10261	23.68
27	1459	3.37
26	513	1.18
19	464	1.07
18	86396	199.34
17	18562	42.83
16	1110	2.56
15	383	0.88
13	580	1.34

million of the P^{31} resonances are reported in Tables 10 to 12. The chemical shifts, δ , in parts per million and coupling constants, J , in hertz of the B^{11} resonances are reported in Table 13. The integrated intensities of the H^1 spectra correspond well with the expected values. The borane hydrogens were not resolved in the H^1 spectra due to broadening by the boron quadrupole moment. The integrations in the region 0-5 ppm did reflect their presence in the baselines. Proton, P^{31} and B^{11} nmr spectra were extremely useful in characterizing the compounds and in studying various reactions.

The coupling patterns in the H^1 spectra of the various alkyl groups of the phosphoranes are what is expected for their corresponding structures. One special addition to these patterns, however, is long range coupling from the phosphorus atom of spin one half (27). This coupling is seen to the α and β protons through three and four bonds respectively. The phosphorus coupling constant to the α protons is on the order of between 15.39 and 24.54 Hz and to the β protons is on the order of between 1.04 and 1.54 Hz. The H^1 nmr spectra of N-methylimino, N-tert-butyylimino and β -N-dimethylaminoiminotriphenylphosphoranes have been reported by Kaplan et al. (27), and their results agree well with the data presented in this study.

In general, there is a definite upfield chemical shift in the resonances of the protons attached to the α and γ carbon atoms of the ligand on coordination to BH_3 . The

Table 10. Proton and P^{31} NMR Data of N-Alkylimino- and β -N-Substituted-Aminoimino-Triphenylphosphoranes.

Compounds	1H Resonances δ , ppm and Coupling Constants J, Hz			P^{31} Resonances δ , ppm
	δ_1	δ_2	δ_3	
$(C_6H_5)_3PN(CH_3)$	2.902 $J_{P-H} = 24.54$ Hz			7.413-7.765 -7.954
$(C_6H_5)_3PN(C_2H_5)$	3.149 $J_{1-2} = 7.04$ Hz $J_{P-H} = 19.54$ Hz	1.168 $J_{2-1} = 7.04$ Hz $J_{P-H} = 1.54$ Hz		7.359-7.762 -3.559
$(C_6H_5)_3PN(n-C_3H_7)$	3.038 $J_{1-2} = 7.08$ Hz $J_{P-H} = 17.01$ Hz	1.500 $J_{1-2} = 7.08$ Hz $J_{2-3} = 7.14$ Hz	0.875 $J_{3-2} = 7.14$ Hz	7.403-7.754 -3.668
$(C_6H_5)_3PN(i-C_3H_7)$	3.356 $J_{1-2} = 6.16$ Hz $J_{P-H} = 19.84$ Hz	1.078 $J_{2-1} = 6.16$ Hz $J_{P-H} = 1.04$ Hz		7.379-7.779 0.515
$(C_6H_5)_3PN(i-C_4H_9)$	2.867 $J_{1-2} = 6.47$ Hz $J_{P-H} = 15.39$ Hz	1.594 $J_{2-1} = 6.47$ Hz $J_{2-3} = 6.59$ Hz	0.897 $J_{3-2} = 6.59$ Hz	7.403-7.761 -3.495
$(C_6H_5)_3PN(t-C_4H_9)$	1.162 $J_{P-H} = 1.22$ Hz			7.377-7.874 14.053
$(C_6H_5)_3PNN(CH_3)_2$	2.329			7.377-7.823 -15.570

Continued

Table 10. Continued.

Compounds	¹ H Resonances δ , ppm and Coupling Constants J, Hz			³¹ P Resonances δ , ppm
	δ_1	δ_2	δ_3	
(C ₆ H ₅) ₃ PNNH(C ₆ H ₅)	5.541 J _{P-H} = 4.15 Hz			7.381-7.941 -18.933 6.567-7.197
(C ₆ H ₅) ₃ PNNCH ₃ (C ₆ H ₅)	3.061 J _{P-H} = .49 Hz			7.381-7.975 -14.624 6.612-7.326

Note: All the δ values represent the centers of the resolvable or complex multiplets; ¹H spectra were run in deuterated methylene chloride; ³¹P spectra were run proton decoupled in benzene; H¹ chemical shifts are measured relative to tetramethylsilane, internal, and P³¹ with respect to 85% phosphoric acid, external; ³¹P shifts are reported with negative shifts downfield from 85% phosphoric acid.

Table 11. Proton and ^{31}P NMR Data of N-Alkylimino- and β -N-Substituted-Aminoimino-Triphenylphosphorane Boranes.

Compounds	^1H Resonances δ , ppm and Coupling Constants J , Hz			Aromatics δ , ppm	^{31}P Resonances δ , ppm
	δ_1	δ_2	δ_3		
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{CH}_3)\text{BH}_3$	2.626 $J_{\text{P-H}}=15.26\text{Hz}$			7.352-7.885	-36.095
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{C}_2\text{H}_5)\text{BH}_3$	2.903 $J_{1-2}=7.00\text{Hz}$ $J_{\text{P-H}}=18.09\text{Hz}$	1.093 $J_{1-2}=7.00\text{Hz}$		7.360-7.903	-34.691
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{n-C}_3\text{H}_7)\text{BH}_3$	2.777 $J_{\text{AB}}=J_{\text{AB}'}=7.57\text{Hz}$ $J_{\text{AA}'}=J_{\text{BB}'}=0.89\text{Hz}$ $J_{\text{P-H}}=16.73\text{Hz}$	1.642 $J_{\text{AB}}=J_{\text{AB}'}=7.57\text{Hz}$ $J_{\text{AA}'}=J_{\text{BB}'}=0.89\text{Hz}$ $J_{2-3}=7.38\text{Hz}$	0.652	7.361-7.910	-34.908
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{i-C}_3\text{H}_7)\text{BH}_3$	3.034 $J_{1-2}=6.50\text{Hz}$ $J_{\text{P-H}}=15.30\text{Hz}$	1.255 $J_{2-1}=6.50\text{Hz}$		7.417-7.885	-32.449
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{i-C}_4\text{H}_9)\text{BH}_3$	2.615 $J_{1-2}=7.10\text{Hz}$ $J_{\text{P-H}}=12.77\text{Hz}$	2.281 $J_{2-1}=7.10\text{Hz}$ $J_{2-3}=6.68\text{Hz}$	0.692	7.414-7.881	-35.239
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{t-C}_4\text{H}_9)\text{BH}_3$	1.198 $J_{\text{P-H}}=0.49\text{Hz}$			7.366-7.912	-23.013

Continued

Table 11. Continued.

Compounds	¹ H Resonances δ , ppm and Coupling Constants J, Hz			³¹ P Resonances δ , ppm
	δ_1	δ_2	δ_3	
(C ₆ H ₅) ₃ PNN(CH ₃) ₂ BH ₃	2.435		7.359-7.812	-36.413
(C ₆ H ₅) ₃ PNNH(C ₆ H ₅)BH ₃	5.080		7.325-7.928	-40.236**
	J _{P-H} =2.93Hz			6.676-7.176
(C ₆ H ₅) ₃ PNN(CH ₃)(C ₆ H ₅)BH ₃	3.133		7.407-7.932	-41.117
			6.614-7.220	

Note: All the δ values represent the centers of the resolvable or complex multiplets;

¹H spectra were run in deuterated methylene chloride; ³¹P spectra were run proton decoupled in benzene; ¹H chemical shifts are measured relative to tetramethylsilane, internal, and ³¹P with respect to 85% phosphoric acid, external; ³¹P shifts are reported with negative shifts downfield from 85% phosphoric acid; *¹H nmr obtained at 300 MHz; **³¹P nmr obtained at 80.984 MHz.

Table 12. Proton and ^{31}P NMR Data of Bis-(N-Alkyliminotriphenylphosphorane) BH_2^+I^- Salts.

Compounds	^1H Resonances δ , ppm and Coupling Constants J, Hz			^{31}P Resonances δ , ppm*
	δ_1	δ_2	δ_3	
$[(\text{C}_6\text{H}_5)_3\text{PN}(\text{CH}_3)_2\text{BH}_2^+]_2\text{I}^-$	2.431 $J_{\text{P-H}}=14.77\text{Hz}$		7.538-7.745	-43.354
$[(\text{C}_6\text{H}_5)_3\text{PN}(\text{C}_2\text{H}_5)_2\text{BH}_2^+]_2\text{I}^-$	2.809 $J_{1-2}=6.98\text{Hz}$ $J_{\text{P-H}}=21.36\text{Hz}$	0.496 $J_{2-1}=6.98\text{Hz}$	7.263-7.832	-41.543
$[(\text{C}_6\text{H}_5)_3\text{PN}(\text{n-C}_3\text{H}_7)_2\text{BH}_2^+]_2\text{I}^-$	2.621 $J_{\text{AB}}=J_{\text{AB}'}=8.39\text{Hz}$ $J_{\text{AA}'}=J_{\text{BB}'}=1.70\text{Hz}$ $J_{\text{P-H}}=21.07\text{Hz}$	0.949 $J_{\text{AA}'}=J_{\text{BB}'}=1.70\text{Hz}$ $J_{2-3}=7.26\text{Hz}$	7.246-8.083 $J_{3-2}=7.26\text{Hz}$	-41.731

Note: All the δ values represent the centers of the resolvable or complex multiplets;

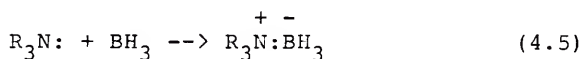
^1H spectra were run in deuterated methylene chloride; ^{31}P spectra were run proton decoupled in benzene; ^1H chemical shifts are measured relative to tetramethylsilane, internal, and ^{31}P with respect to 85% phosphoric acid, external; ^{31}P shifts are reported with negative shifts downfield from 85% phosphoric acid; * ^{31}P nmr obtained at 80.984 MHz.

Table 13. B^{11} NMR Data of Borane Adducts and Boron Cations.

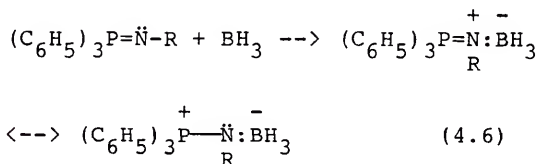
Compounds	Chemical Shift δ , ppm	Multiplicity	J_{B-H} Hz
$(C_6H_5)_3PN(CH_3)BH_3$	33.981	4	88.53
$(C_6H_5)_3PN(C_2H_5)BH_3$	35.520	4	84.59
$(C_6H_5)_3PN(n-C_3H_7)BH_3$	35.104	4	84.74
$(C_6H_5)_3PN(i-C_3H_7)BH_3$	39.498	4	82.76
$(C_6H_5)_3PN(i-C_4H_9)BH_3$	35.792	4	86.49
$(C_6H_5)_3PN(t-C_4H_9)BH_3$	35.142	4	88.54
$(C_6H_5)_3PNN(CH_3)_2BH_3$	44.173	4	91.74
$(C_6H_5)_3PNNH(C_6H_5)BH_3$	35.472*	4	66.24
$(C_6H_5)_3PNN(CH_3)(C_6H_5)BH_3$	40.299	1	**
$[(C_6H_5)_3PN(CH_3)]_2BH_2I^-$	25.842*	1	**
$[(C_6H_5)_3PN(C_2H_5)]_2BH_2I^-$	29.715*	1	**
$[(C_6H_5)_3PN(n-C_3H_7)]_2BH_2I^-$	27.513*	1	**

Note. All the δ values represent the proton decoupled peaks; B^{11} spectra were run in methylene chloride; B^{11} chemical shifts are measured relative to trimethylborate, external; B^{11} shifts are reported with negative shifts downfield from trimethylborate; * B^{11} nmr obtained at 64.184 MHz; ** coupling in these peaks was complete collapsed by quadrupole relaxation.

resonances of the protons attached to the β carbon atom of the ligand show a shift downfield on coordination to BH_3 . The upfield chemical shift of the α proton resonances on coordination to BH_3 is just the opposite of what is seen with amine boranes (15). When amines are coordinated to BH_3 , a positive formal charge is assigned to the nitrogen atom, and thus a downfield shift for the protons closest to the nitrogen is expected.



When N-alkyliminotriphenylphosphoranes are coordinated to BH_3 , a positive charge is also assigned to the nitrogen atom. In this case, however, a resonance structure can be drawn placing the positive charge on the less electronegative phosphorus atom. This would cause a shift upfield for the proton resonances due to the buildup of electrons on the nitrogen atom.



A general decrease of the long range phosphorus coupling constant is observed in the proton resonances of the ligand on coordination to BH_3 . A decrease in the

phosphorus coupling constant is also seen upon protonation and methylation of the nitrogen atom (27), and in these respects the behavior on BH_3 coordination is analogous.

The H^1 nmr spectrum of N-n-propyliminotriphenylphosphorane borane is noteworthy because the coupling pattern of the n-propyl group is non-first order. The coupling pattern falls into the special category of A_2B_2 (69). This type of coupling pattern is sometimes seen with n-propyl groups. The spin coupling of identical protons leads to the A_2B_2 case. The symmetry and coupling constants are represented in Figure 9.

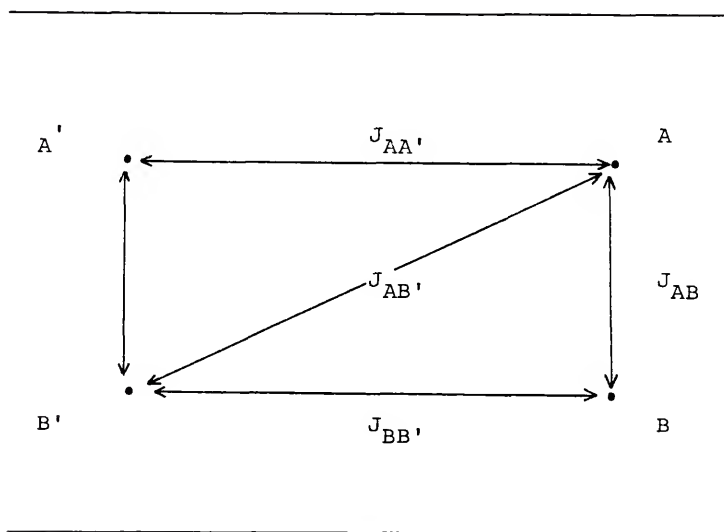


Figure 9. Symmetry and coupling constants of the A_2B_2 case.

There are four coupling constants, $J_{AA'}$, J_{AB} , $J_{AB'}$, and $J_{BB'}$. Because of symmetry, $J_{A'B} = J_{AB}$, and $J_{A'B'} = J_{AB'}$. To simplify solving the various coupling constants, four new quantities are defined: $K = J_{AA'} + J_{BB'}$; $L = J_{AB} - J_{AB'}$; $M = J_{AA'} - J_{BB'}$; and $N = J_{AB} + J_{AB'}$. A much simpler subcase of A_2B_2 is A_2X_2 in which the chemical shift between A and X is large compared to the various coupling constants. This is the case in the spectrum of N-n-propyliminotriphenylphosphorane borane. The A and B parts will be identical minus coupling from the phosphorus and from the methyl protons. There should be ten lines in each of the two parts, and each part will be symmetrical about its center. The line positions and intensities are given in Table 14 (70).

The A part of the pattern will be treated first. The coupling pattern of the A protons, the protons attached to the α carbon atom, is reproduced in Figure 10. In general, the pattern consists of a quintet split into two by the phosphorus coupling. The line positions in hertz and intensities of the ten lines along with the line positions, minus the phosphorus coupling constant, are given in Table 15.

From the spectrum, only five peaks besides the phosphorus coupling, and not the expected ten, are observed for the A part. In order to collapse ten peaks into five, some assumptions can be made. Assuming that $J_{AA'} = J_{BB'}$, and that

Table 14. Line Positions and Intensities for the A_2X_2 Case.

Transition	Position Relative to V_A or V_X	Relative Intensity
1	$1/2 N$	1
2	$1/2 N$	1
3	$-1/2 N$	1
4	$-1/2 N$	1
5	$1/2 K + 1/2 (K^2 + L^2)^{1/2}$	$\sin^2 \theta_s$
6	$-1/2 K + 1/2 (K^2 + L^2)^{1/2}$	$\cos^2 \theta_s$
7	$1/2 K - 1/2 (K^2 + L^2)^{1/2}$	$\cos^2 \theta_s$
8	$-1/2 K - 1/2 (K^2 + L^2)^{1/2}$	$\sin^2 \theta_s$
9	$1/2 M + 1/2 (M^2 + L^2)^{1/2}$	$\sin^2 \theta_a$
10	$-1/2 M + 1/2 (M^2 + L^2)^{1/2}$	$\cos^2 \theta_a$
11	$1/2 M - 1/2 (M^2 + L^2)^{1/2}$	$\cos^2 \theta_a$
12	$-1/2 M - 1/2 (M^2 + L^2)^{1/2}$	$\sin^2 \theta_a$

$$\theta_s = 1/2 \cos^{-1} [K / (K^2 + L^2)^{1/2}]$$

$$\theta_a = 1/2 \cos^{-1} [M / (M^2 + L^2)^{1/2}]$$

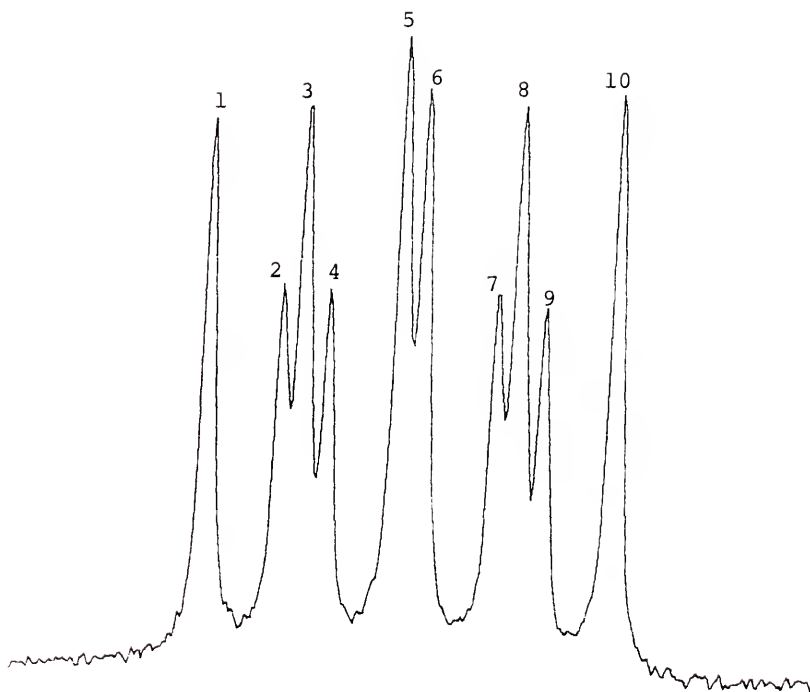


Figure 10. Expansion of α protons in H^1 nmr spectrum of N-n-propyliminotriphenylphosphorane borane.

Table 15. Line Positions of the α Protons.

Position of Lines in Part A Hz		Intensity	Position of Lines in Part A Minus Phosphorus Coupling Hz	
1)	849.27	462.87		
2)	843.47	325.78		
3)	841.84	474.89	1)	840.93
4)	839.91	322.21	5)	835.09
5)	834.20	535.11		833.48
6)	832.59	492.01	8)	831.53
7)	826.70	320.87	3)	825.86
8)	825.11	478.98		
9)	823.15	310.49		
10)	817.51	490.21		

$J_{AB} = J_{AB'}$, then both M and L are equal to zero, and five peaks result. The rest of the calculation is as follows:

$$1) - 3) = 1/2 N - (-1/2 N) = N$$

$$1) - 3) = 15.07 \text{ Hz} = N = J_{AB} + J_{AB'}$$

$$J_{AB} = J_{AB'} = 7.535 \text{ Hz}$$

$$5) - 8) = K - (-K) = 2K$$

$$5) - 8) = 3.55 \text{ Hz} = 2K$$

$$K = J_{AA'} + J_{BB'} = 1.78 \text{ Hz}$$

$$J_{AA'} = J_{BB'} = 0.888 \text{ Hz}$$

The B part of the pattern will be treated next. The coupling pattern of the B protons, the protons attached to the β carbon atom, is reproduced in Figure 11. A selective decoupling experiment was performed by irradiating the methyl protons to collapse their coupling in the B part. The resulting coupling pattern is reproduced in Figure 12. In general, the pattern consists of the expected quintet. The peak positions in hertz and intensities of the five lines are given in Table 16.

The calculation for the B part is as follows:

$$1) - 3) = 15.21 \text{ Hz} = N = J_{AB} + J_{AB'}$$

$$J_{AB} = J_{AB'} = 7.605 \text{ Hz}$$

$$5) - 8) = 3.59 \text{ Hz} = 2K$$

$$K = J_{AA'} + J_{BB'} = 1.80 \text{ Hz}$$

$$J_{AA'} = J_{BB'} = 0.900 \text{ Hz}$$

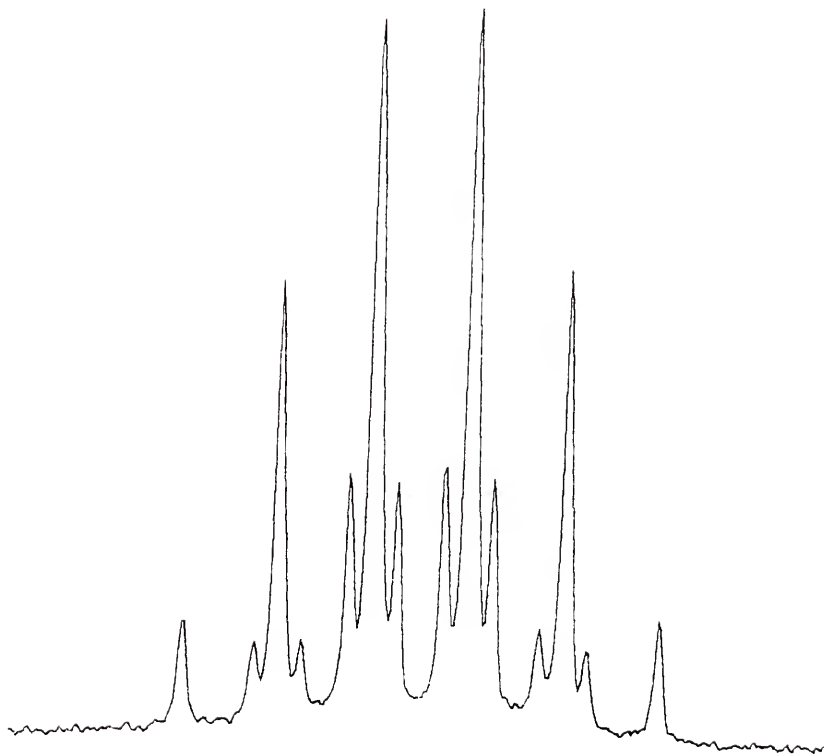


Figure 11. Expansion of β protons in H^1 nmr spectrum of N-n-propyliminotriphenylphosphorane borane.

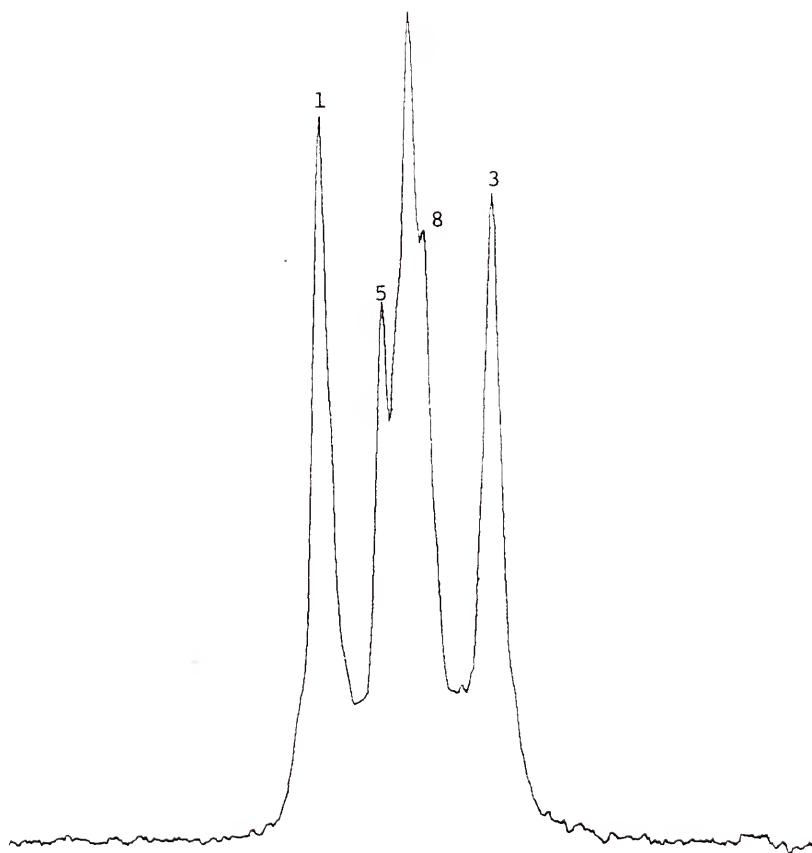


Figure 12. Expansion of β protons, decoupled from methyl protons, in H^1 spectrum of N-n-propylimino-triphenylphosphorane borane.

Table 16. Line Positions of the B Part.

	Position of Lines Hz [*]	Intensity
1)	-761.18	257.07
5)	-766.70	191.87
	-769.08	292.89
8)	-770.29	216.96
3)	-776.39	229.57

* The values are relative to an unknown reference.

The values for the coupling constants calculated for parts A and B agree well with each other, as expected. Average values for J_{AB} , $J_{AB'}$, $J_{AA'}$, and $J_{BB'}$ are reported in Table 11. The spectrum of N-n-propyliminotriphenylphosphorane is reproduced in Figure 13 as an example for proton spectra of the phosphoranes. The spectrum of N-n-propyliminotriphenylphosphorane borane is reproduced in Figure 14 as an example for proton spectra of the borane adducts.

In general, there is a definite upfield chemical shift in the resonances of the alkyl protons of the ligand on going from borane adduct to boron cation. Since a positive charge is assigned to the boron containing unit, an enhancement of the delocalization of positive charge to the phosphorus atoms could explain the observed phenomenon. A

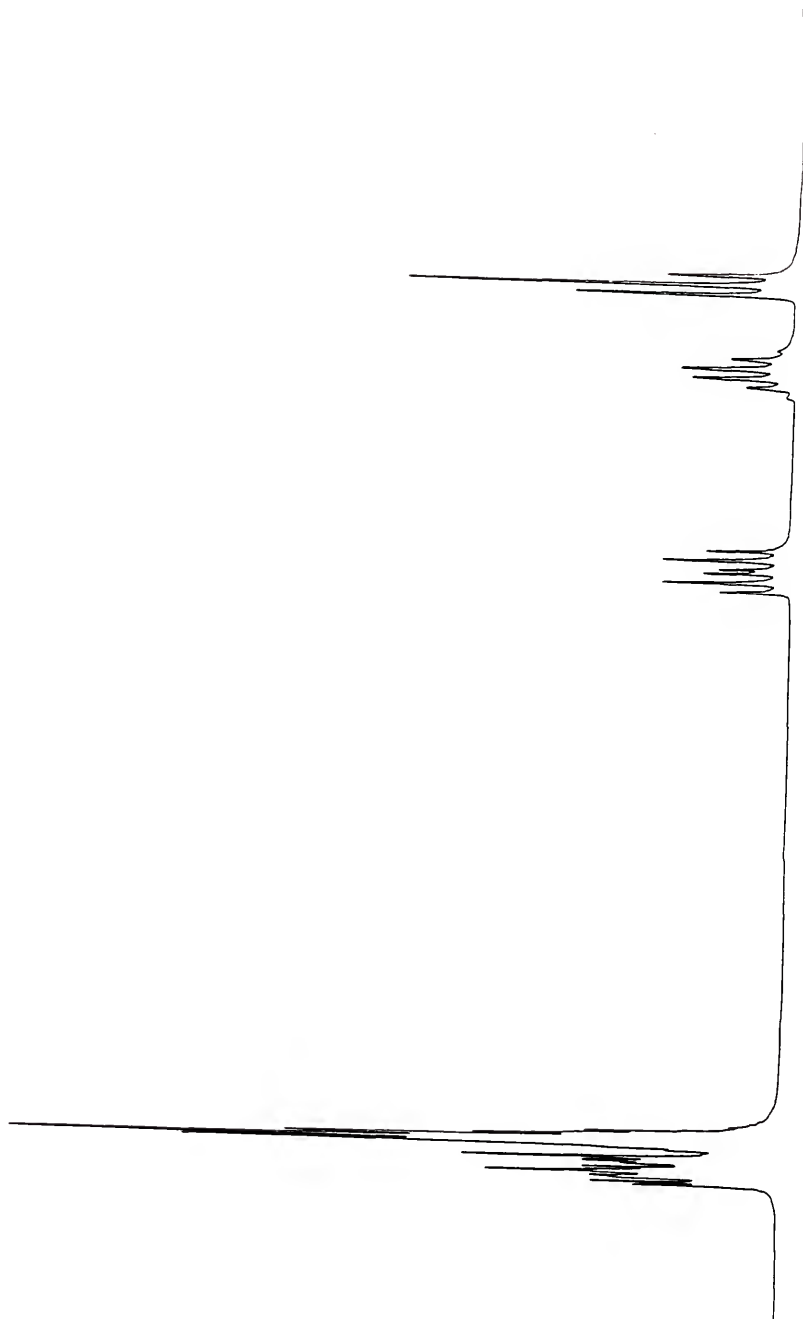


Figure 13. ^1H nmr spectrum of N-n-propyliminotriphenylphosphorane.

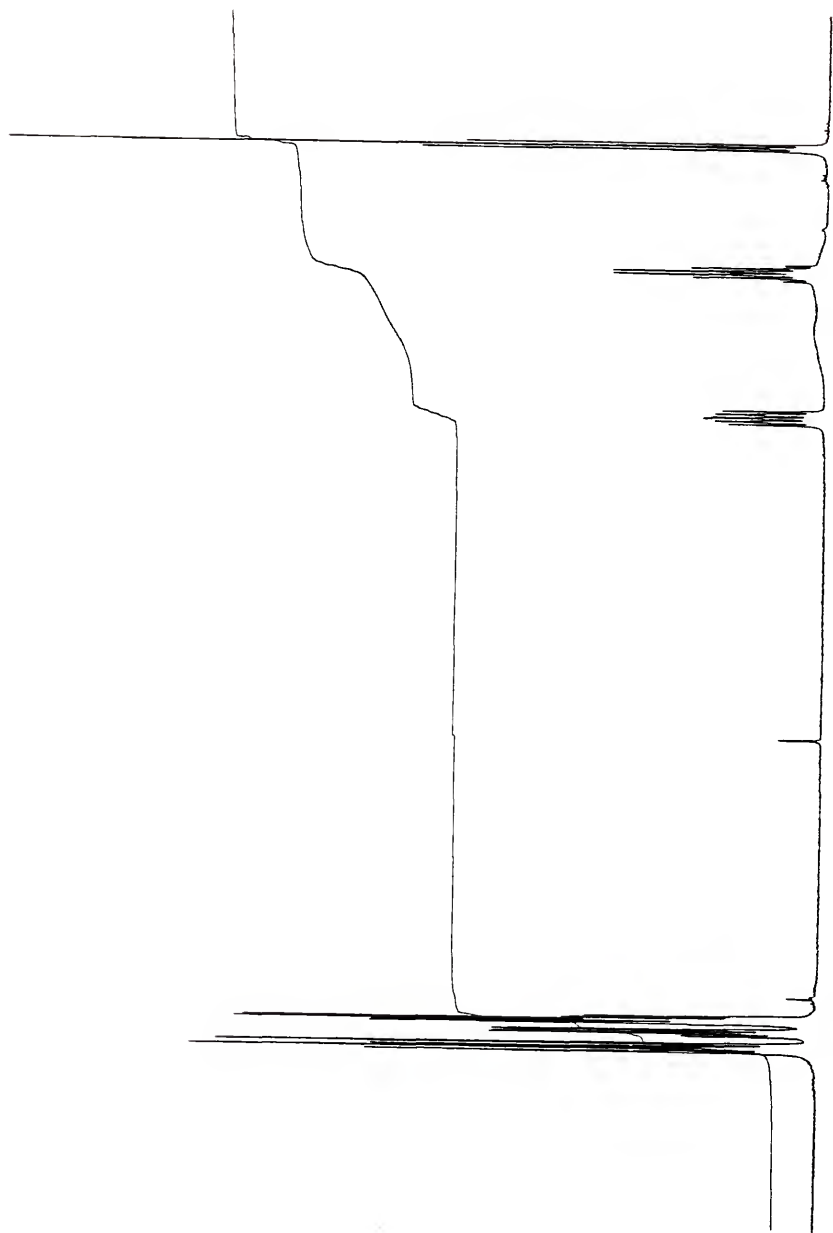


Figure 14. ^1H nmr spectrum of N-n-propyliminotriphenylphosphorane borane.

change in the spatial positions of the alkyl groups cannot be overlooked, however, due to the various ring currents from the phenyl groups.

The H^1 nmr spectrum of bis(N-n-propyliminotriphenylphosphorane) boronium iodide also exhibits an A_2B_2 coupling pattern. The same treatment described for the corresponding borane adduct was used to solve for the various coupling constants. The spectrum of bis(N-ethyliminotriphenylphosphorane) boronium iodide is reproduced in Figure 15 as an example for proton spectra of the boron cations.

In general, the B^{11} resonances are quartets, with varying degrees of collapse, for all the borane adducts, as expected. Boron-11 nuclei, with a spin of $3/2$, possess an electric quadrupole moment due to nonsphericity of the electric charge distribution within the nucleus. These nuclei interact with the fluctuating electric field gradients produced at the nucleus by other molecular degrees of freedom. These interactions lead to smaller values of T_1 , the spin-lattice relaxation time (70). Since the line width measured on a frequency scale is proportional to $1/T_1$, then smaller values of T_1 lead to broadening of the line. If a boron nucleus is coupled to another spin nucleus, simple multiplets will occur in the absence of quadrupolar relaxation. If the rate of relaxation of the boron nucleus becomes rapid enough, the multiplet will coalesce into a broad signal.

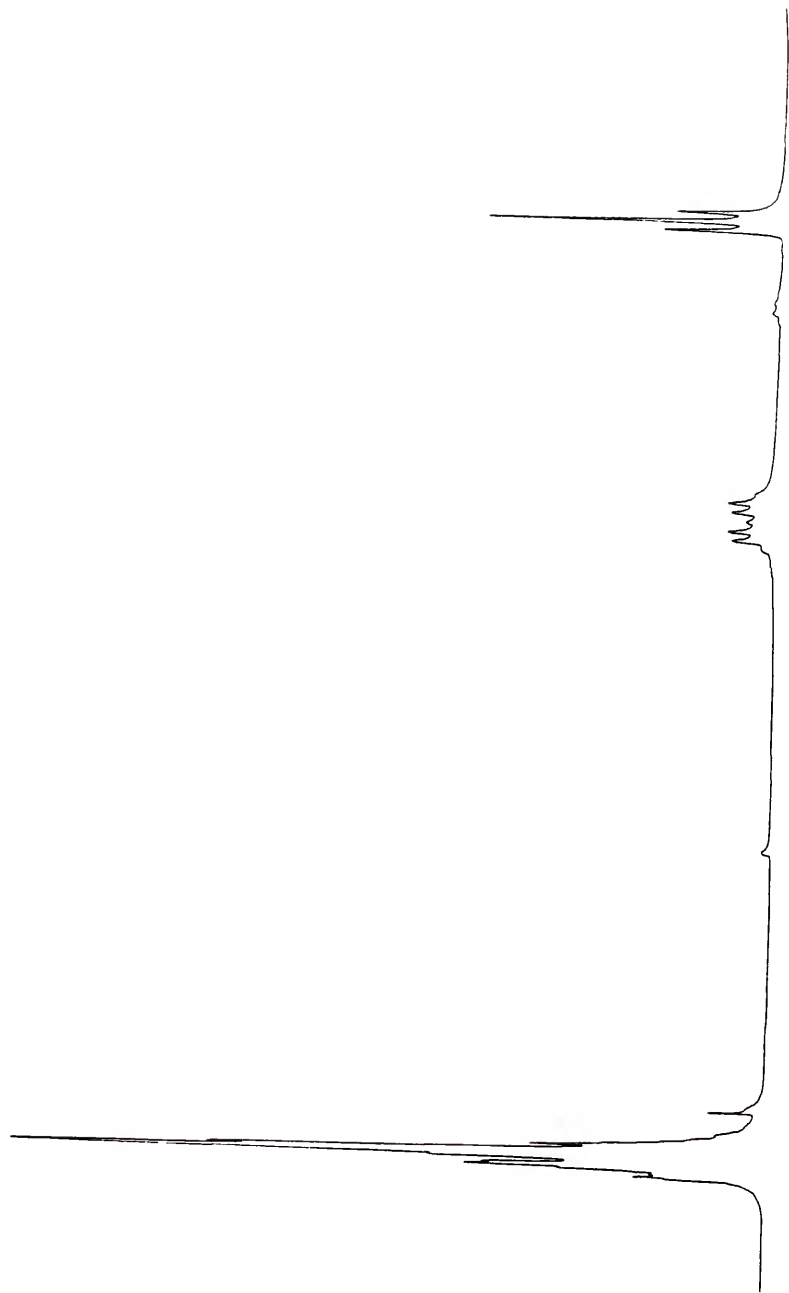


Figure 15. ^1H nmr spectrum of bis-(N-ethyliminotriphenylphosphorane)boronium iodide.

Saji (71) studied this phenomenon in amine boranes. Theoretical results predict that for slow quadrupole relaxation, the spectrum consists of individual lines equally broadened, and that for smaller relaxation times, the maxima of inner peaks move inward until all four coalesce into a doublet. Experimental results show that quadrupole relaxation is not the only mechanism of spin-lattice relaxation and that dipole-dipole interactions may have a significant contribution. Measured spectra of substituted pyridine boranes show that the outer resonances decrease in intensity and move inward as the inner resonances increase in intensity and move outward.

The same types of results were seen for the B^{11} resonances of the borane adducts. All of the boron spectra were also run proton decoupled to see if any coupling between the phosphorus-31 and boron-11 nuclei could be observed. The proton decoupled spectra were broad singlets with half-widths of approximately 89 Hz. Starzewski and Dieck (72) report C^{13} nmr spectra of a number of N-alkyl-iminotriphenylphosphoranes. Their data show phosphorus coupling constants to the α carbon atom of the alkyl groups on the order of between 32.2 and 51.7 Hz. Assuming that the coupling constants from phosphorus to boron are of the same order of magnitude, the coupling would be undetectable using conventional nmr and would only lead to broadening of the peak.

The proton decoupled B^{11} nmr spectrum of N-methylimino-triphenylphosphorane borane is reproduced in Figure 16 as an example of a proton decoupled spectrum. The proton coupled B^{11} nmr spectra of N-methylimino, N-ethylimino, β -N-phenyl-aminoimino and β -N-methyl,phenylaminoiminotriphenylphosphorane boranes are reproduced in Figures 17-20 as examples of B^{11} spectra of the borane adducts.

The B^{11} nmr spectra of the boronium iodides are extremely broad peaks that show no multiplicity. The resonances are expected to be triplets for the BH_2^+ group, but the quadrupole relaxation has completely collapsed the coupling. The broad peaks do not appear to change significantly when the protons are decoupled. The chemical shift of the B^{11} resonances in BH_2^+ is in the range of 25-30 ppm, while in the borane adducts it is in the range of 33-44 ppm. Thus, as expected, there is a definite downfield shift in the B^{11} resonances of the cations compared to the corresponding borane adducts. The B^{11} chemical shifts of the bis(N-alkyliminotriphenylphosphorane) boronium iodides are noticeably further upfield than for the bis-amine cations (29,35-37). The proton coupled and decoupled spectra of bis(N-n-propyliminotriphenylphosphorane) boronium iodide are reproduced in Figures 21 and 22 respectively as examples of B^{11} spectra of the boronium cations.

The P^{31} nmr spectra proton decoupled are sharp well resolved singlets. In general, there is a definite downfield chemical shift in the resonances of the phosphorus

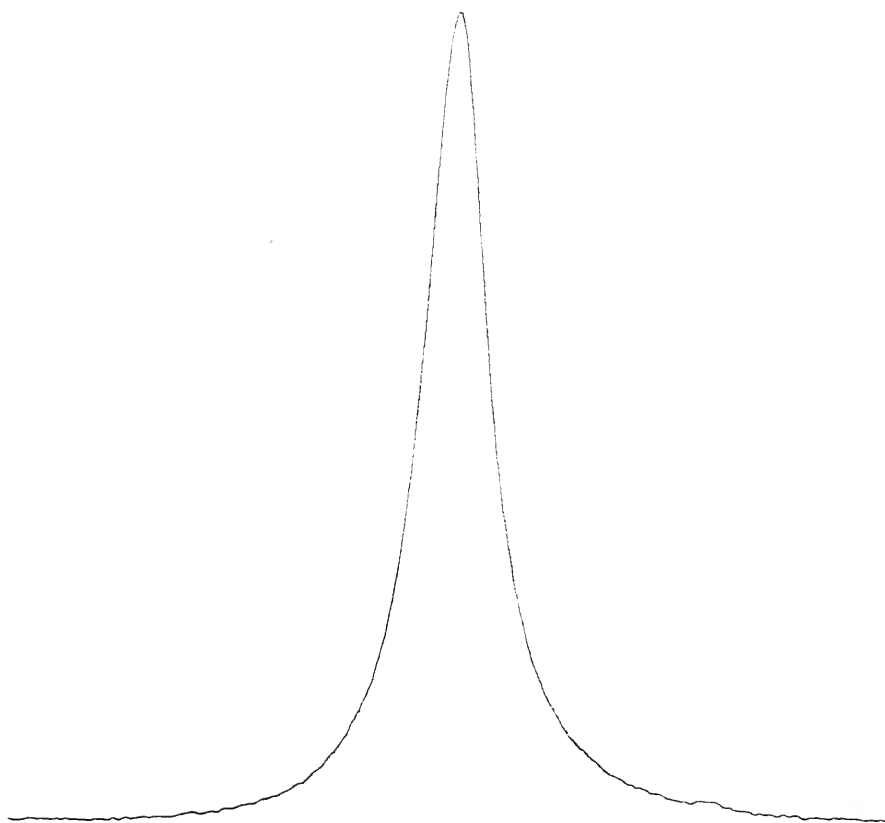


Figure 16. Proton decoupled B^{11} nmr spectrum of N-methyl-
iminotriphenylphosphorane borane.

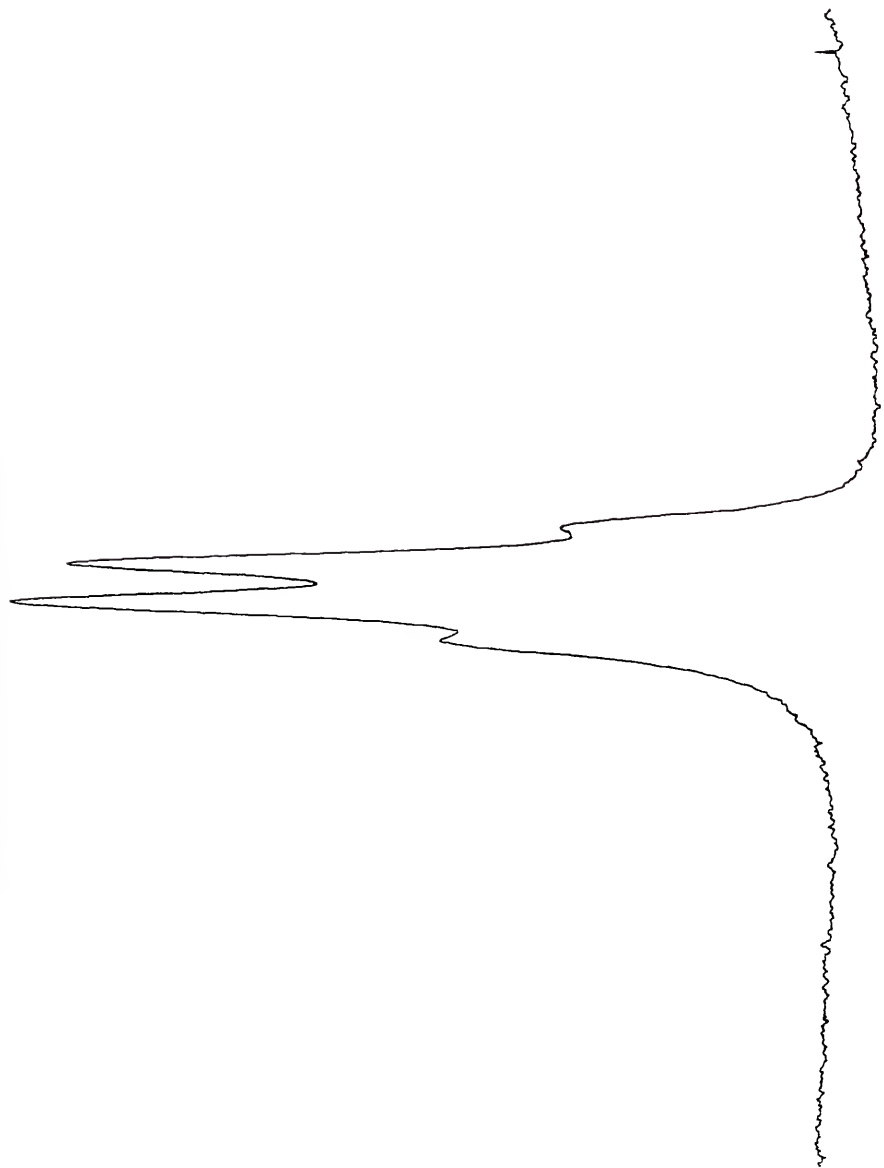


Figure 17. Proton coupled ^{11}B nmr spectrum of N-methyliminotriphenylphosphorane borane.

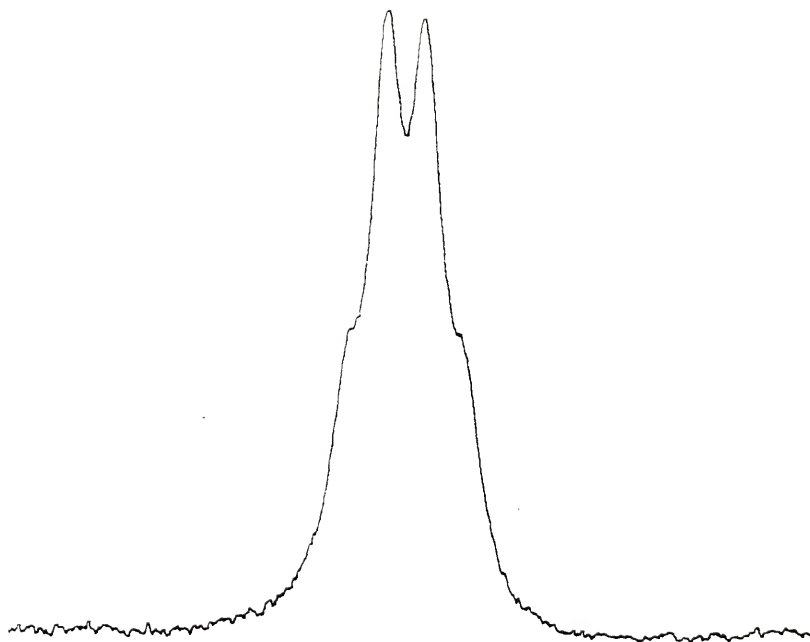


Figure 18. Proton coupled B^{11} nmr spectrum of N-ethylimino-triphenylphosphorane borane.

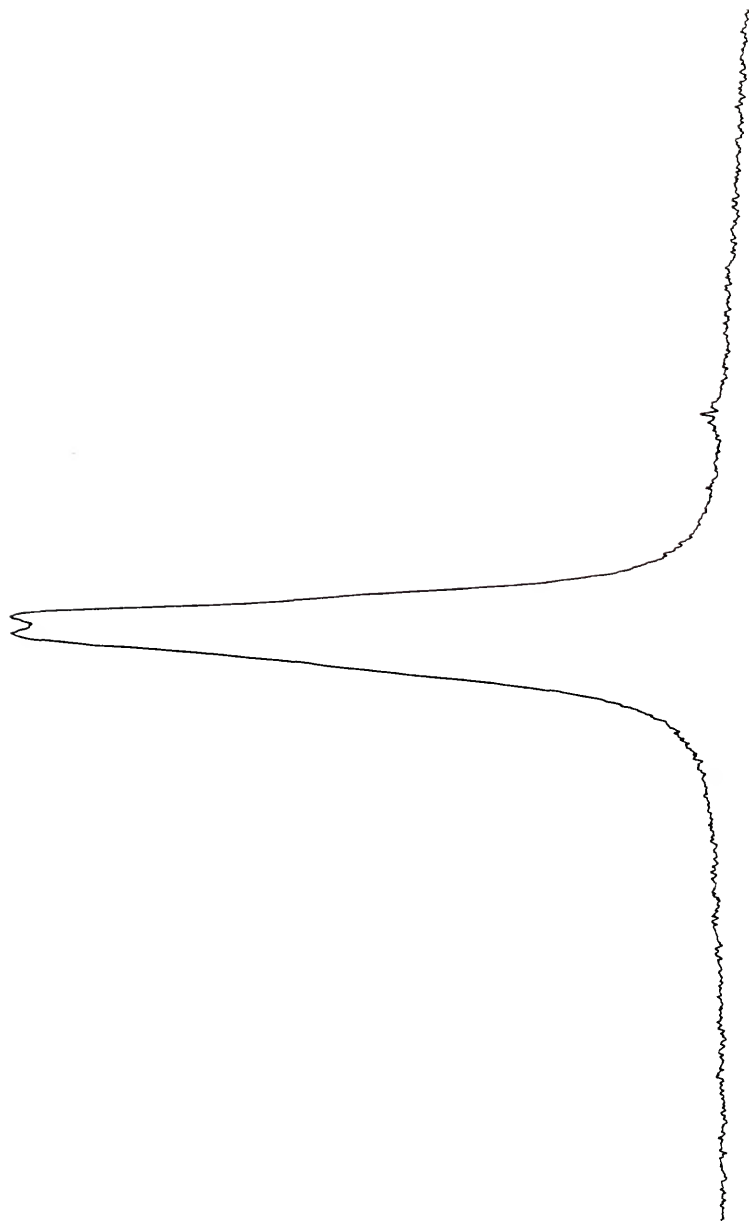


Figure 19. Proton coupled ^{11}B nmr spectrum of β -N-phenylaminoiminotriphenylphosphorane borane.

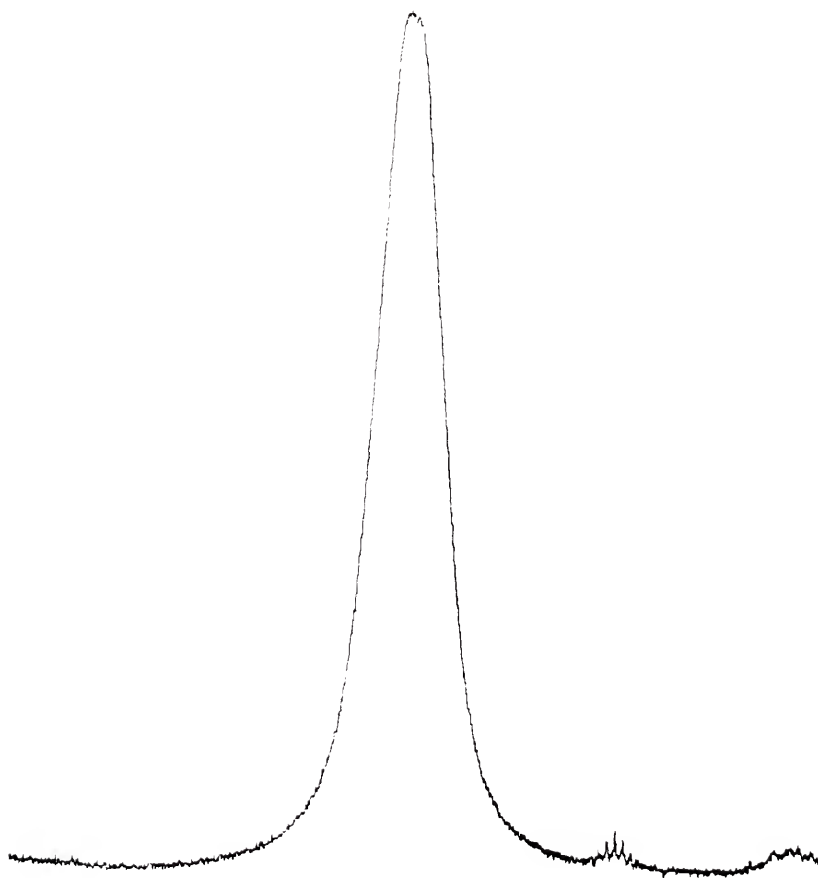


Figure 20. Proton coupled B^{11} nmr spectrum of β -N-methyl, phenylaminoiminotriphenylphosphorane borane.

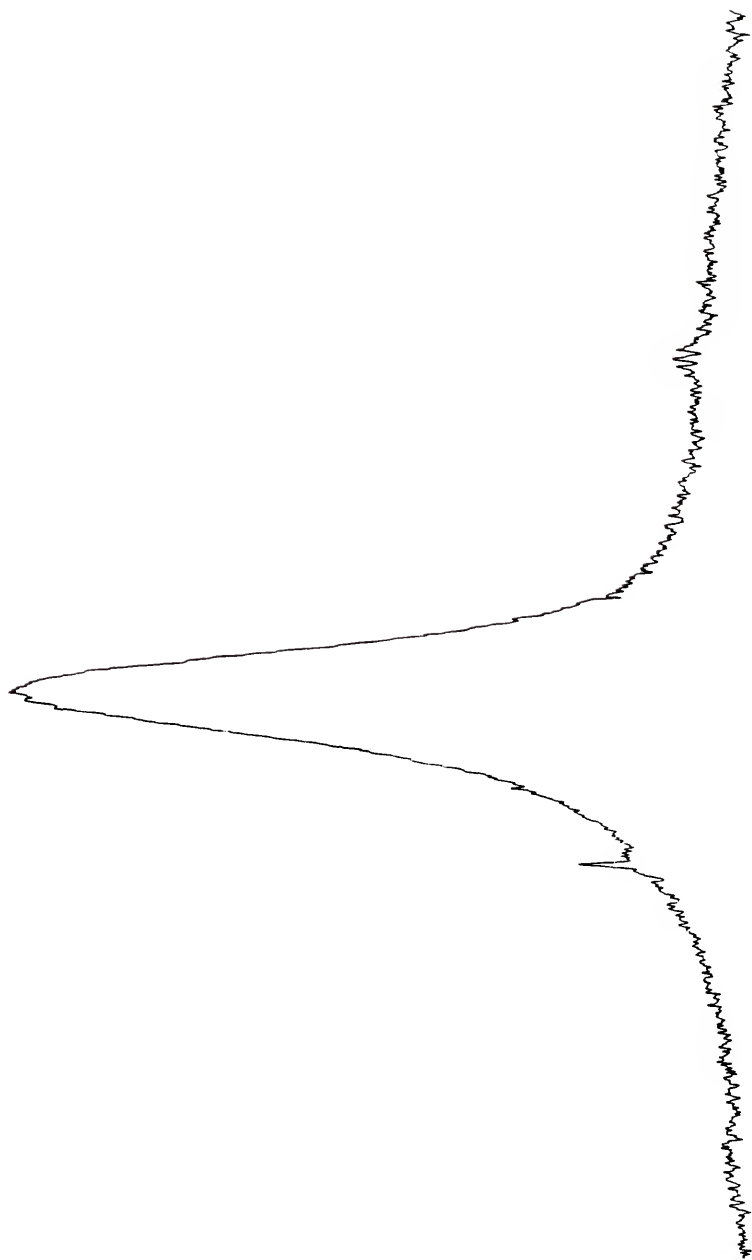


Figure 21. Proton coupled B^{11} nmr spectrum of bis-(N-n-propyliminotriphenylphosphorane)boronium iodide.

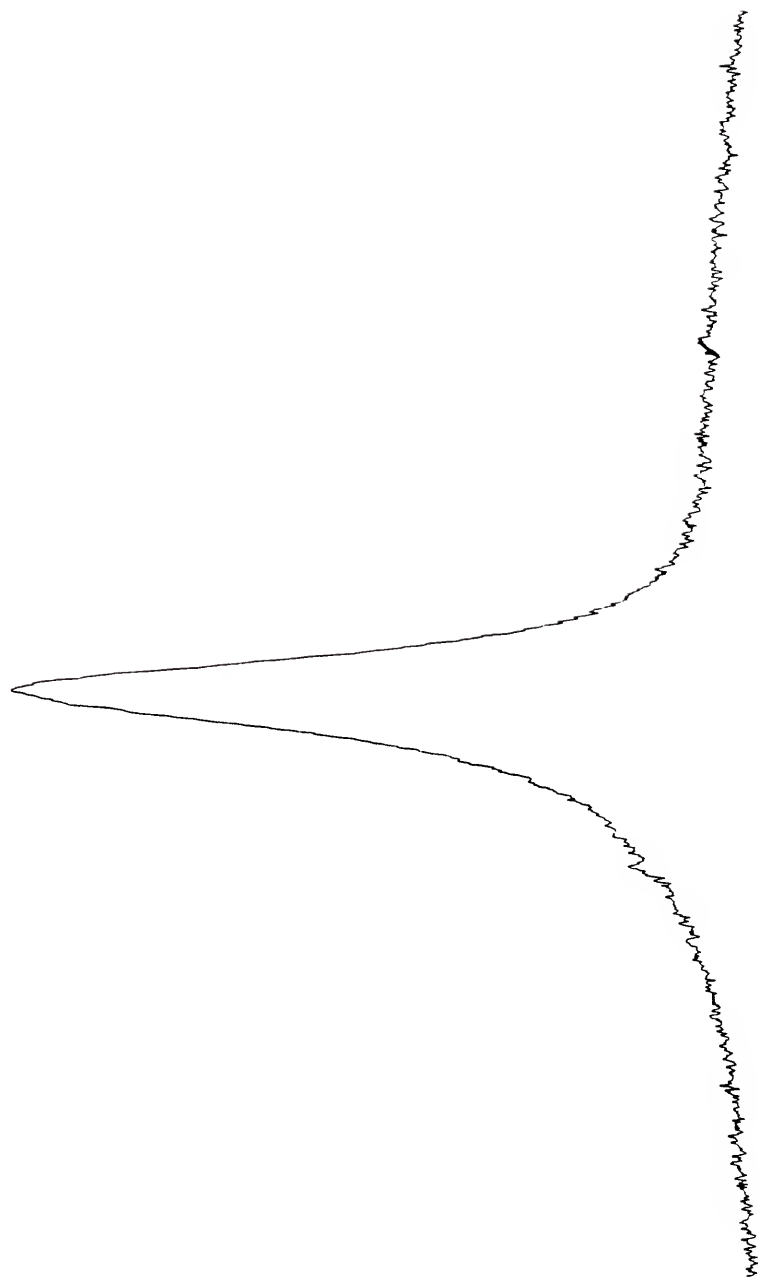


Figure 22. Proton decoupled ^{11}B nmr spectrum of bis(N-n-propyliminotriphenylphosphorane)boronium iodide.

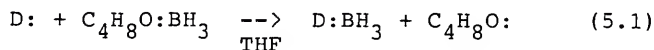
atoms of the ligand on going from phosphorane to borane adduct to boron cation, as expected from the increase in positive charge on the phosphorus.

CHAPTER V

DISCUSSION ON SYNTHESES OF BORANE ADDUCTS AND BORON CATIONS

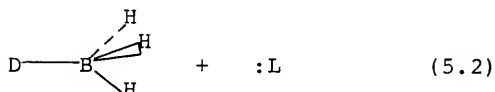
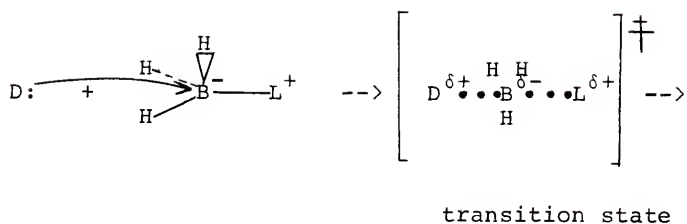
Syntheses of Borane Adducts

Two different general synthetic methods were used to produce borane adducts. The first procedure employed displacement of a donor coordinated to BH_3 (2,11) using the borane-tetrahydrofuran complex and an N-substituted-imino-triphenylphosphorane. The results of this synthetic method show that it is a convenient and rapid procedure that produces borane adducts in essentially quantitative yields according to the following equation.



The reaction proceeded quickly at room temperature, and products of fairly good purity were obtained.

Two different mechanisms are possible for nucleophilic substitution on tetrahedral boron. The first to be considered is $\text{S}_\text{N}2$. The nucleophile approaches and by donation of its electron pair forms a partial bond to boron while the leaving group boron bond begins to break as illustrated in the following equation.



Backside attack must consist of transfer of electron density from the nucleophile HOMO into the substrate LUMO, which is an antibonding σ orbital between the boron and the leaving group. This interaction will stabilize the transition state so that the reaction can occur. Interaction of the nucleophile HOMO with the substrate LUMO is represented in the following figure.

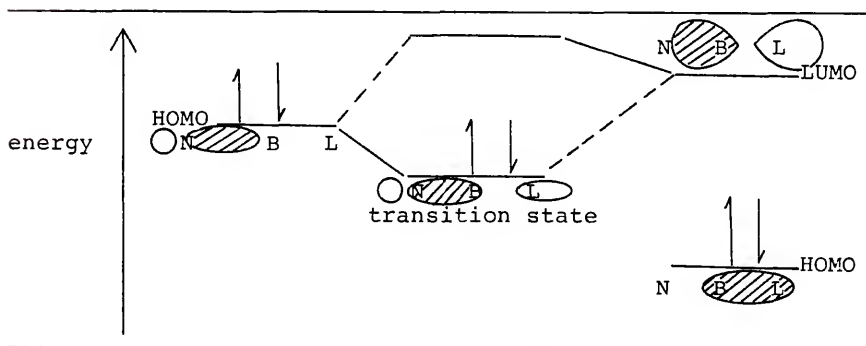


Figure 23. HOMO-LUMO interaction in $\text{S}_{\text{N}}2$ mechanism.

Assignment of formal charges in the borane-tetrahydrofuran complex places a negative charge on the boron atom and a positive charge on the oxygen atom. The negative formal charge on the boron atom should cause electrostatic repulsion toward the nucleophile lone pair of electrons. Thus, a S_N2 mechanism would be expected to have a high activation energy. The high activation energy would reduce the probability of a S_N2 mechanism occurring.

The second mechanism to be considered is S_N1 . In this case the boron to oxygen bond cleaves heterolytically and free BH_3 is formed. Then, in a second step, the nucleophile attacks this highly reactive intermediate. The second step would proceed by a transfer of electron density from the nucleophile HOMO into the substrate LUMO, which is a non-bonding p orbital on the boron. The interaction is represented in the following figure.

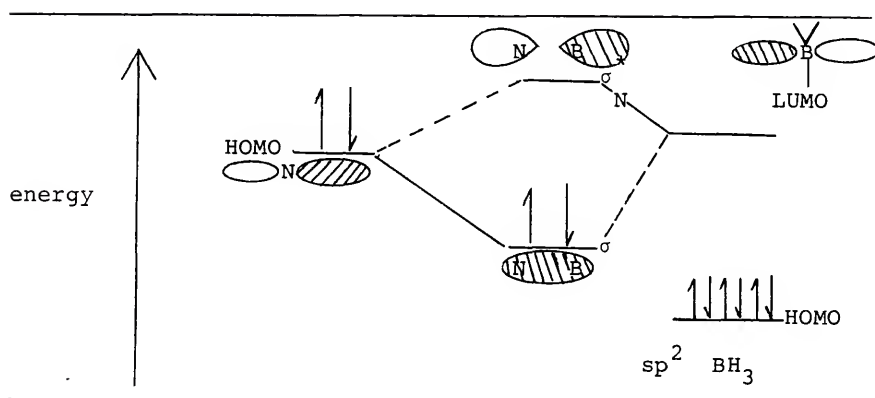


Figure 24. HOMO-LUMO interaction in S_N1 mechanism.

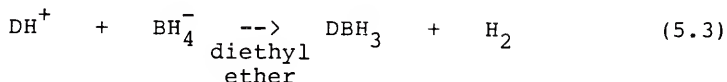
The result is a σ bond between the nucleophile and the boron atom.

One other step is possible in the S_N1 mechanism. This step would involve the reaction of two BH_3 units to form B_2H_6 . Since there is a large excess of tetrahydrofuran molecules present, the first step in the S_N1 mechanism is thought of as an equilibrium, with only very small amounts of free BH_3 produced. Thus, the probability of two BH_3 units finding each other is quite small. Boron-11 nmr spectra of borane-tetrahydrofuran solutions show no evidence for the presence of molecular diborane (73,74).

The activation energy of the equilibrium step would be the boron to oxygen coordinate bond energy. The second step in the S_N1 mechanism should have a lower activation energy than the first step, making the equilibrium step the rate determining one. If the activation energy in the S_N2 mechanism is less than the activation energy of the rate determining step in the S_N1 mechanism, then the reaction would proceed through S_N2 and vice versa. In the absence of any kinetic data for the reaction, no conclusion, as to which mechanism operates, can be made.

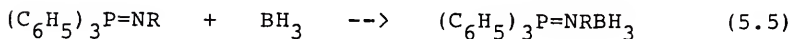
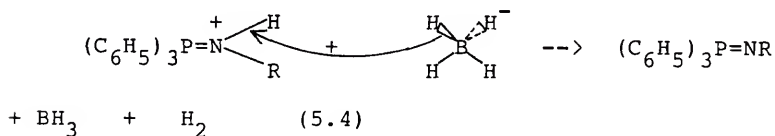
The second method employed to produce borane adducts was reaction of a N-substituted-aminotriphenylphosphonium bromide with lithium borohydride in diethyl ether. The procedure was similar to that reported by Schaeffer and Anderson (13) in the preparation of trimethylamine borane. The results of this synthetic method show that it is also a

convenient and rapid preparation that proceeds according to the following equation.



The reaction proceeded quickly at room temperature. Hydrogen evolution ceased after 2 hours, and external heating was applied to ensure that the reaction was completed.

Since diethyl ether is a very poor proton acceptor, the reaction mechanism must occur by abstraction of hydride by phosphonium ion followed by addition of the nitrogen lone pair.



After hydride abstraction, the nitrogen lone pair and the BH_3 unit should be in very close proximity to each other. Therefore, diffusion away from the reaction site by either molecule before complexation can occur is highly unlikely.

The reaction of the iminium ions with borohydride demonstrates that these ions behave in the same way that ammonium ions do.

A comparison of the two methods in Table 3 shows that both procedures are synthetically useful in the production of borane adducts. The first method has the advantage of being quicker, and the workup is much simpler than in the second method. However, the first method employs the use of isolated phosphoranes which are difficult and time consuming to prepare from their hydrobromide salts. The second procedure employs the use of phosphonium bromides and produces the corresponding phosphoranes in situ. This reduces the total preparation time by eliminating the phosphorane isolation procedure. Although the yield is lower in the second method, this procedure appears to be the preferred route to the borane adducts of N-substituted-iminotriphenylphosphoranes.

Borane adducts of the β -N-substituted-aminoimino-triphenylphosphoranes were prepared by method one using three times the stoichiometric amount of BH_3 required for mono addition. The β -N-substituted-aminoiminotriphenylphosphoranes have two basic lone pairs available for complexation by BH_3 . The experimental results show that only one BH_3 unit per molecule is added. This is evidenced by a combination of elemental analyses and proton decoupled ^{11}B nmr data. The proton decoupled ^{11}B nmr spectra all show only one singlet each.

The behavior of these molecules toward BH_3 parallels their behavior toward methylation. Zimmer and Singh (20) found that these compounds react with only one mole of methyl iodide at the α nitrogen atom.

After addition of the first mole of BH_3 , a compound with a positive formal charge on the coordinated nitrogen is produced. Two factors must be considered to explain why a second mole of BH_3 does not attach itself to the molecule. Steric hindrance by the attached BH_3 unit may shield the basic lone pair from attack. The second factor to be considered is charge communication. The positive formal charge on the coordinated nitrogen atom could create a larger effective nuclear charge on the uncoordinated nitrogen atom. This would have the effect of contracting the lone pair of electrons closer to the nucleus and thus reduce their basicity. The same type of reasoning can be used to explain why only one mole of methyl iodide was added. In this case, however, the charge communication is much greater due to the positive charge on the ion.

The question of which nitrogen atom is attached to the BH_3 can be answered by the following reasoning. Coordination of the β nitrogen atom by BH_3 would not change the P^{31} nmr chemical shift significantly from that of the free base. Coordination of the α nitrogen atom by BH_3 would cause a substantial shift downfield in the P^{31} nmr resonance relative to the uncoordinated base. Comparisons of the P^{31} nmr

shifts of the β -N-substituted-aminoiminotriphenylphosphoranes and their borane adducts reveal that shifts on the order of 20 ppm downfield are observed upon coordination by BH_3 .

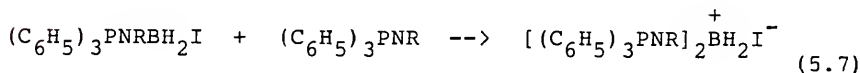
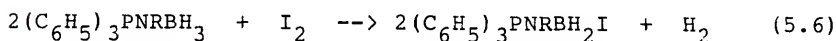
The $\text{N}(\text{CH}_3)_2$ group is structurally similar to the isopropyl group. Coordination of the α nitrogen atom of β -N-dimethylaminoiminotriphenylphosphorane by BH_3 would be expected to show a shift in the methyl resonance similar to that seen in the methyl resonance of N-isopropyliminotriphenylphosphorane upon coordination by BH_3 . A shift in the methyl resonances in the H^1 nmr spectra of 0.18 and 0.11 ppm are seen upon coordination by BH_3 of N-isopropyliminotriphenylphosphorane and β -N-dimethylaminoiminotriphenylphosphorane respectively.

Coordination of the β nitrogen atom of β -N-dimethylaminoiminotriphenylphosphorane by BH_3 would be expected to produce a substantial broadening of the methyl resonance from the boron quadrupole moment. It was observed that the linewidth of the methyl resonance of the free base was not substantially different from the linewidth of the methyl resonance of the corresponding borane adduct.

From the observed behavior in the P^{31} and H^1 nmr spectra of the β -N-substituted-aminoiminotriphenylphosphoranes upon coordination by BH_3 , it was concluded that the α nitrogen atom must be the site of coordination.

Synthesis of Boron Cations

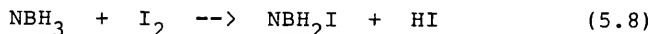
The symmetrical boron cations reported in Chapter III (Table 4) were prepared by nucleophilic substitution reactions on an in situ prepared iodoborane. Solutions of N-alkyliminotriphenylphosphorane boranes in benzene were allowed to react with stoichiometric amounts of iodine. The iodoborane solutions were then allowed to react with the corresponding phosphorane at room temperature, and thus boronium salts were prepared. The general reaction sequence can be represented by the following equations.



R = methyl, ethyl, n-propyl

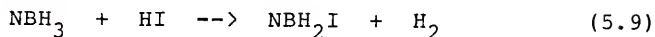
The syntheses of the new cations proceeded rapidly, and high yields were obtained.

In general, the borane adducts were found to be quite reactive toward iodination. The reaction can be visualized to take place by the following steps.

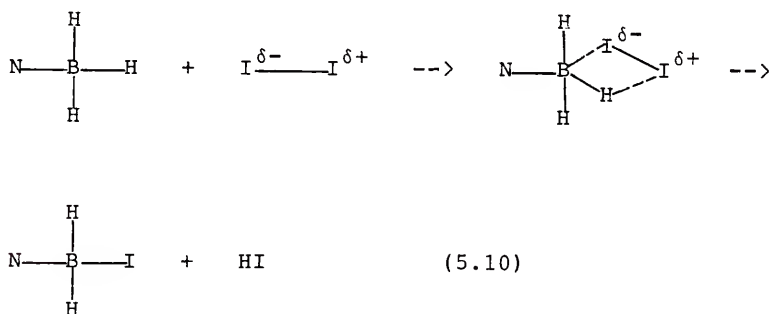


where N=phosphorane.

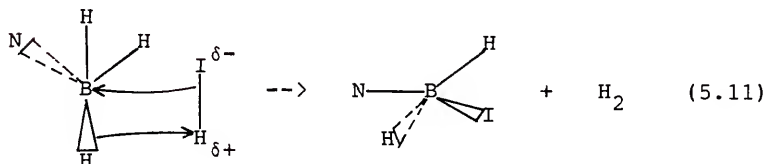
The HI generated could immediately react with more borane to produce monoiodoborane.



Nöth and Beyer (52) explain the first step in the iodination sequence as a polarization of the attacking iodine molecule by the boron atom as $\text{I}^{\delta-}-\text{I}^{\delta+}$. The negative end of the molecule then attacks the slightly positive boron atom while the positive end attacks the hydride.



Assuming strictly anhydrous conditions, the reaction of HI on borane can then follow a concerted one step process as follows:



The iodoboranes were used immediately after they were prepared and were not isolated. Attempts to isolate iodoboranes of the phosphoranes produced sticky, oily materials which defied workup.

In general, iodoboranes of the N-alkyliminotriphenylphosphoranes were found to be more reactive than trimethylamine iodoborane. Although no specific kinetic experiments were performed in this research project, it was observed that N-n-propyliminotriphenylphosphorane iodoborane was much more reactive than trimethylamine iodoborane toward the same nucleophile. For example, a very large amount of precipitate was observed after 10 minutes of stirring in the reaction of N-n-propyliminotriphenylphosphorane iodoborane with N-n-propyliminotriphenylphosphorane, while solutions of trimethylamine iodoborane with the same nucleophile showed no visible precipitate after 2 hours of reaction.

The difference between the reactivities of the two iodoboranes can be attributed to steric and electronic factors. The nitrogen atom in trimethylamine iodoborane is sp^3 hybridized. This would produce a B-N-C bond angle of approximately 109° . The nitrogen atoms in N-alkyliminotriphenylphosphorane iodoboranes are sp^2 hybridized. This would produce a B-N-C bond angle of approximately 120° . Assuming backside attack of the nucleophile on the boron atom in a Sn_2 mechanism, the alkyl group of trimethylamine iodoborane would be closer to the nucleophile and cause more steric hindrance toward attack than the alkyl group of the

sp^2 hybridized nitrogen. Thus, the methyl groups of the sp^3 nitrogen would cause the activation energy of the transition state to be raised, and the reactivity would be lowered.

Electronic factors may also play an important part in explaining differences in reactivity. In the transition state of a $Sn2$ reaction, the boron atom being attacked is sp^2 hybridized. The other p orbital is used to conjugate with the $d_{\pi}-p_{\pi}$ electron system of the P-N bond plus participate in bonding to the incoming nucleophile and the iodide group (see Figure 25). The conjugation can be viewed as a delocalization of the positive charge, formed during the transition state, to the phosphorus atom. This interaction would stabilize the transition state and consequently increase the reaction rate. The same sort of arguments were used to explain the increased reactivity of substituted pyridine iodoboranes over alkylamine iodoboranes (29).

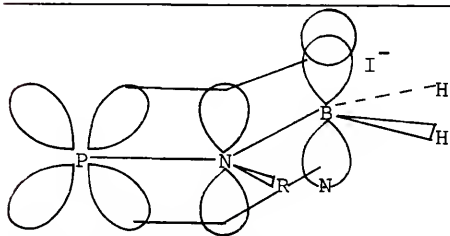
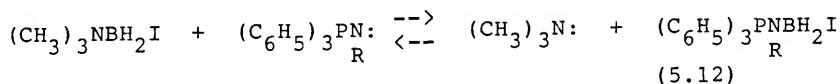


Figure 25. Transition state for $Sn2$ reaction on $(C_6H_5)_3PNRBH_2I$.

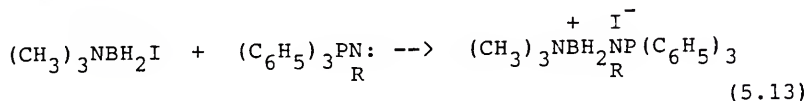
Only one attempt was made to prepare an unsymmetrical boron cation, namely, the reaction between trimethylamine iodoborane and N-n-propyliminotriphenylphosphorane. The products of this reaction were found to be a mixture of symmetrical boron cations in equimolar proportions. No evidence for the production of an unsymmetrical cation was observed. This result is interesting in that during the production of unsymmetrical cations, employing alkylamines and substituted pyridines as ligands, symmetrical cations were reported as not being in the products (37).

Since equimolar amounts of the symmetrical cations were produced, any mechanism explaining this phenomenon must include cleavage of a B-N bond to produce free trimethylamine. Three different reaction sequences can be used to produce free trimethylamine. These are represented by the following equations.

Sequence 1



Sequence 2

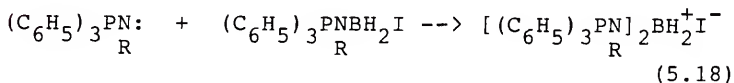
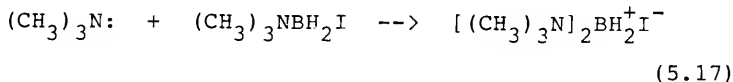


research program show that N-n-propyliminotriphenylphosphorane is a weaker base than trimethylamine. Thus, sequence 1 is not expected to proceed rapidly.

Bases having similar steric restraints and greater basicities than N-n-propyliminotriphenylphosphorane react with trimethylamine iodoborane to give unsymmetrical cations exclusively (37). Sequences 2 and 3 both include production of the unsymmetrical cation by iodide displacement as the first step. Equation (5.14) produces trimethylamine through a transamination reaction. The transition state of such a reaction would involve a sp^2 hybridized boron atom with the other p orbital being used to bond with the incoming nucleophile and trimethylamine. A transition state such as this would necessarily have two nitrogens from the phosphorane groups at ninety degrees to each other. The nitrogen from the trimethylamine group would also be at ninety degrees to one of the sp^2 hybridized nitrogen atoms. This arrangement would create a very bulky transition state. The steric hindrance involved should raise the activation energy and reduce the probability of this reaction occurring. Equation (5.16) involves a nucleophilic displacement of trimethylamine by iodide ion. The transition state of this reaction would also contain a sp^2 hybridized boron atom. Since iodide is less bulky than N-n-propyliminotriphenylphosphorane, the activation energy for equation (5.16) should be less than the activation energy in equation (5.14). This conclusion, combined with the fact that

iodide ion is a better nucleophile than a sp^2 nitrogen, makes sequence 3 the preferred route to produce trimethylamine.

The trimethylamine produced in the reaction can then react with trimethylamine iodoborane to form bis(trimethylamine) boronium cation represented by equation (5.17). The iodoborane produced can react with N-n-propyliminotriphenylphosphorane to form the corresponding symmetrical cation represented by equation (5.18).



The observation that only equimolar amounts of symmetrical cations were isolated means that the unsymmetrical cation is used up at the same rate that it is formed. Thus, the concentration of the unsymmetrical cation must be low and constant.

Trimethylamine iodoborane has been shown to react with different nucleophiles to produce either, a mixture of symmetrical cations, or an unsymmetrical cation exclusively. The difference in reactivity can be explained by examination of the transition states for trimethylamine displacement by iodide ion on the corresponding unsymmetrical cations. The

transition states for this reaction using (trimethylamine) (pyridine)boronium iodide and (trimethylamine) (N-n-propyl- iminotriphenylphosphorane)boronium iodide are represented in Figures 26 and 27 respectively.

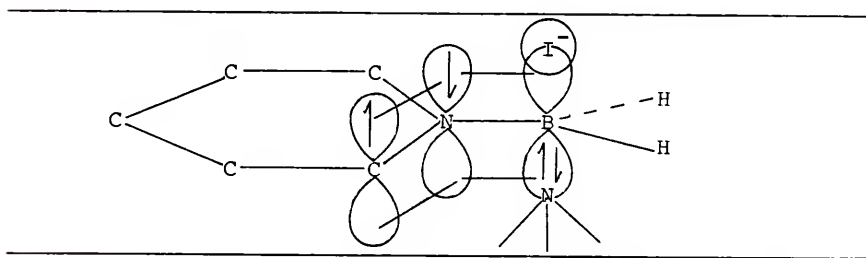


Figure 26. Transition state for trimethylamine displacement in (trimethylamine)(pyridine)boronium iodide.

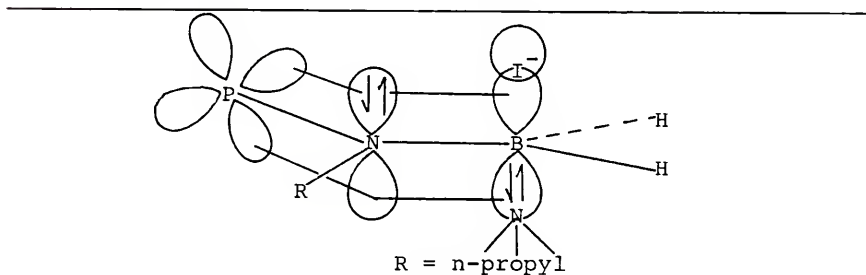


Figure 27. Transition state for trimethylamine displacement in (trimethylamine) (N-n-propyliminotriphenylphosphorane)boronium iodide.

Both transition states have similar steric restraints, and both are stabilized by overlap of the p orbital on boron with a π -bonding system of electrons. The difference in the overlap is seen by the number of electrons in the p orbitals of the sp^2 hybrid nitrogens. The nitrogen in the pyridine system has only one electron that can be donated into the p orbital on the boron atom. However, the nitrogen in the phosphorane system has two electrons in its p orbital that can overlap with the boron p orbital. Therefore, the greater electron density should stabilize the transition state more in the phosphorane example compared to the pyridine analog. This could lower the activation energy for trimethylamine displacement by iodide more in the phosphorane example and thus make the reaction more likely to occur in this molecule.

CHAPTER VI

MEASUREMENT OF EQUILIBRIUM CONSTANTS FOR THE EXCHANGE OF BH_3 BETWEEN N-ALKYLIMINOTRIPHENYLPHOSPHORANES AND BORANE ADDUCTS OF TRIMETHYLAMINE AND 4-METHYLPYRIDINE

A series of experiments were performed to measure the relative base strengths of N-alkyliminotriphenylphosphoranes. The experiments were performed in sealed 5 mm nmr tubes employing solutions of trimethylamine borane or 4-methylpyridine borane with various N-alkyliminotriphenylphosphoranes. The alkyl groups used were methyl, ethyl, n-propyl, isopropyl, isobutyl and tert-butyl. The procedures employed to prepare the nmr tube reactions are represented by the preparation to measure exchange of BH_3 between N-methyliminotriphenylphosphorane and trimethylamine borane.

Preparation to Measure Exchange of BH_3 Between N-Methyliminotriphenylphosphorane and Trimethylamine Borane

Into a 2 ml volumetric flask, N-methyliminotriphenylphosphorane, 0.1237 g (4.246 mmoles), was placed. The flask was filled to the mark with dry benzene. The solid completely dissolved producing a solution that was 0.2123 M in phosphorane. Trimethylamine borane, 0.0840 g (1.15 mmoles),

was placed into a 5 ml volumetric flask. The flask was filled to the mark with dry benzene. The solid completely dissolved producing a solution that was 0.230 M in trimethylamine borane. Approximately one half of a milliliter of each of the solutions was syringed into the same nmr tube. The resulting solution was 0.115 M in trimethylamine borane and 0.106 M in N-methyliminotriphenylphosphorane. A very small amount of tetramethylsilane was added to the contents of the tube, and the tube was sealed with a flame.

All of the other experiments were prepared in the same manner. The approximate starting concentrations of the reactants are listed in Tables 17 and 18. The tubes were kept at 25° for 7 days. Proton or B^{11} nmr spectra of each of the tubes were recorded to determine if exchange had occurred. In those experiments where exchange did occur at 25°, the corresponding tubes were kept at 25° for various periods of time to allow equilibrium to be attained. The tubes were then kept at 50° for various periods of time to allow equilibrium for BH_3 exchange to be reached. Equilibrium constants for exchange were measured by recording H^1 or a combination of proton decoupled B^{11} and P^{31} nmr spectra. Equilibrium constants for exchange were calculated by using the integrated areas under the peaks of interest in the corresponding spectra.

Table 17. Starting Concentrations of Reactants in the Exchange of BH_3 Between N-Alkyliminotriphenylphosphorane and Trimethylamine Borane.

Alkyl Group	$[(\text{C}_6\text{H}_5)_3\text{PNR}]$	$[(\text{CH}_3)_3\text{NBH}_3]$
methyl	0.106 M	0.115 M
ethyl	0.0987 M	0.100 M
n-propyl	0.101 M	0.108 M
isopropyl	0.100 M	0.100 M
isobutyl	0.0985 M	0.100 M
t-butyl	0.100 M	0.100 M

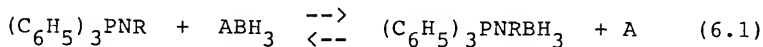
Table 18. Starting Concentrations of Reactants in the Exchange of BH_3 Between N-Alkyliminotriphenylphosphorane and 4-Methylpyridine Borane.

Alkyl Group	$[(\text{C}_6\text{H}_5)_3\text{PNR}]$	$[\text{C}_6\text{H}_7\text{NBH}_3]$
methyl	0.0982 M	0.116 M
ethyl	0.0992 M	0.103 M
n-propyl	0.101 M	0.100 M
isopropyl	0.100 M	0.103 M
isobutyl	0.108 M	0.112 M
t-butyl	0.0991 M	0.103 M

Results and Treatment of Data

Data from experiments in which P^{31} and B^{11} nmr spectra were integrated are presented in Table 19. Data from experiments in which H^1 nmr spectra were integrated are given in Table 20. The relative concentrations reported in this study are expressed as integrated areas and therefore have units of millimeters. In order to arrive at values for the equilibrium constants, some data manipulation was required.

The general reaction describing exchange of BH_3 between a N-alkyliminotriphenylphosphorane and a borane adduct of trimethylamine or 4-methylpyridine is represented in the following equation



where R = methyl, ethyl, n-propyl, isopropyl, isobutyl and tert-butyl.

A = trimethylamine and 4-methylpyridine.

The equilibrium constant for equation (6.1) is expressed as

$$K_{eq} = \frac{[(C_6H_5)_3PNRBH_3][A]}{[(C_6H_5)_3PNR][ABH_3]}$$

Table 19. ^{31}P and ^{11}B NMR Data for Exchange of BH_3 According to
 $(\text{C}_6\text{H}_5)_3\text{PNR} + \text{A}:\text{BH}_3 \xrightarrow{\text{---}} (\text{C}_6\text{H}_5)_3\text{PNRBH}_3 + \text{A}:$

Experiment	Temperature °C	^{31}P Relative Concentrations mm		^{11}B Relative Concentrations mm		Time Days
		Phosphorane	Borane	A: BH_3	Phosphorane Borane	
R = ethyl A = trimethylamine	25	99.6	7.3	80.4	1.6	70
R = ethyl A = trimethylamine	50	88.2	34.0	69.0	27.0	62
R = n-propyl A = trimethylamine	50	47.9	14.5	77.5	12.8	20
R = isopropyl A = trimethylamine	50	85.9	5.3	74.6	6.8	24
R = isobutyl A = trimethylamine	50	47.4	13.5	74.7	4.1	24
R = ethyl A = 4-picoline	25	32.2	17.8	96.2	18.1	63
R = ethyl A = 4-picoline	50	26.1	65.5	32.4	77.7	62
R = isopropyl A = 4-picoline	50	39.4	27.0	103.7	33.9	24
R = isobutyl A = 4-picoline	50	37.6	26.9	49.4	47.1	62

Table 20. H^1 NMR Data for Exchange of BH_3 According to
 $(C_6H_5)_3PNR + A:BH_3 \xrightleftharpoons[A:(C_6H_5)_3PNRBH_3]{} A:$

Experiment	Temperature °C	H^1 Relative Concentrations mm			Time Days
		Phosphorane	Phosphorane Borane	A: BH_3	
R = methyl A = trimethylamine	25	15.4	2.47	7.24	41
R = methyl A = trimethylamine	50	9.1	5.0	3.4	13
R = methyl A = 4-picoline	25	74.6	139.9	37.6	70
R = methyl A = 4-picoline	50	30.0	149.8	28.4	9
R = n-propyl* A = 4-picoline	50	16.0	22.0	14.9	10

* Recorded at 300 MHz.

Since the areas under the peaks of interest are proportional to the concentrations of the species they represent, areas were substituted for the concentrations in the equilibrium expression. In this way equilibrium constants were calculated. The H^1 nmr spectra required the greatest amount of data treatment. Consequently, data treatment of each experiment, in which H^1 nmr was used to measure the equilibrium constant, will be described fully.

Data Manipulation in the Exchange of BH_3 Between N-Methyl-
iminotriphenylphosphorane and Trimethylamine Borane

Equilibrium constants at 25° and 50° were measured using integrated areas of peaks in the H^1 nmr spectra. Expansions of the integrated peaks of interest are presented in Figures 28 and 29 corresponding to 25° and 50° respectively. Examination of Figures 28 and 29 reveals that four broad peaks corresponding to $3/4$ of a proton each, from the BH_3 group of trimethylamine borane, are present in each spectrum. These peaks represent protons bonded to the B^{11} isotope which is 81.1% of naturally occurring boron. One of these peaks occurs under the methyl resonances of N-methyl-
iminotriphenylphosphorane borane, and one occurs under the trimethylamine borane resonance. The area under one of the BH_3 peaks was integrated, and this area was subtracted from the area under the methyl resonances of the phosphorane borane. The corrected area, as well as the area under the methyl resonances of the phosphorane, were divided by three

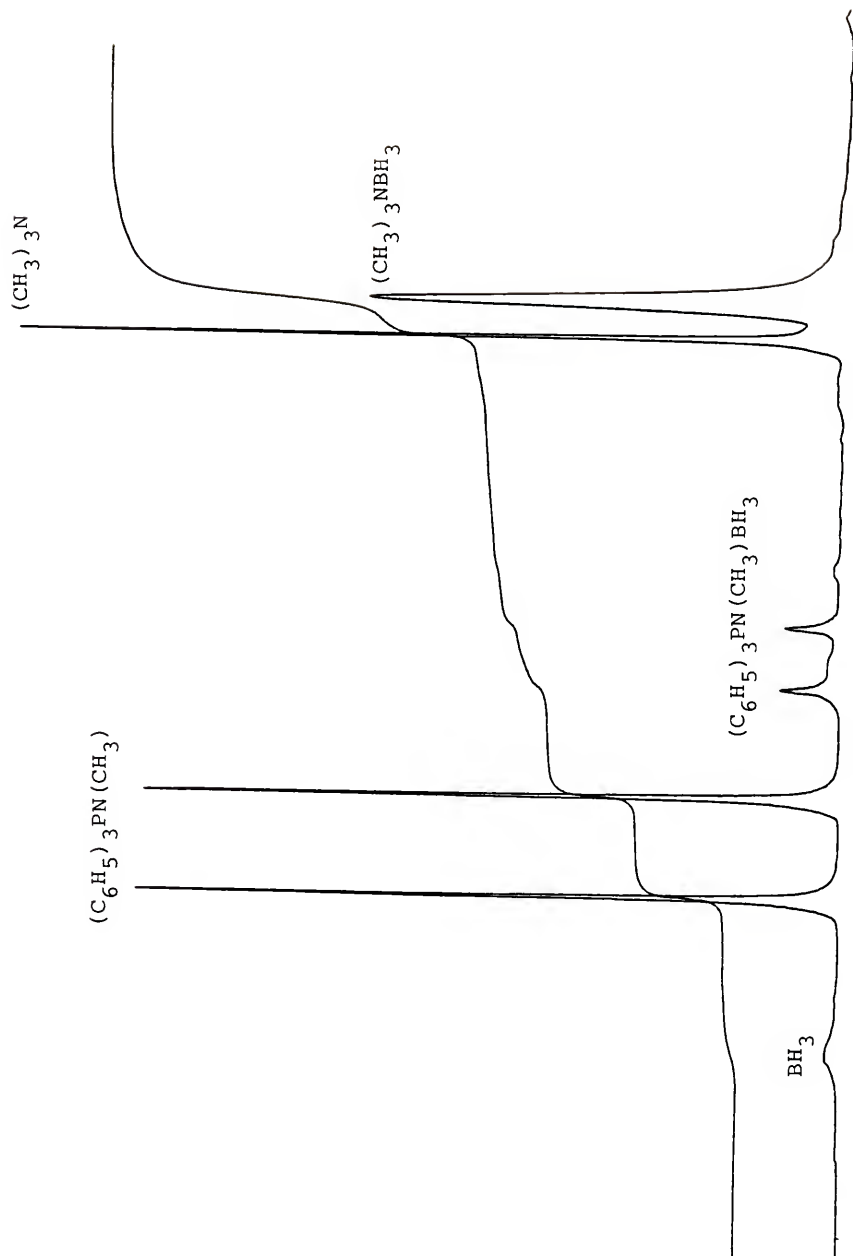


Figure 28. Expansion of ^1H nmr spectrum for exchange of BH_3 between $\text{N-methylimino-triphenylphosphorane}$ and $\text{trimethylamine borane}$ at 25° .

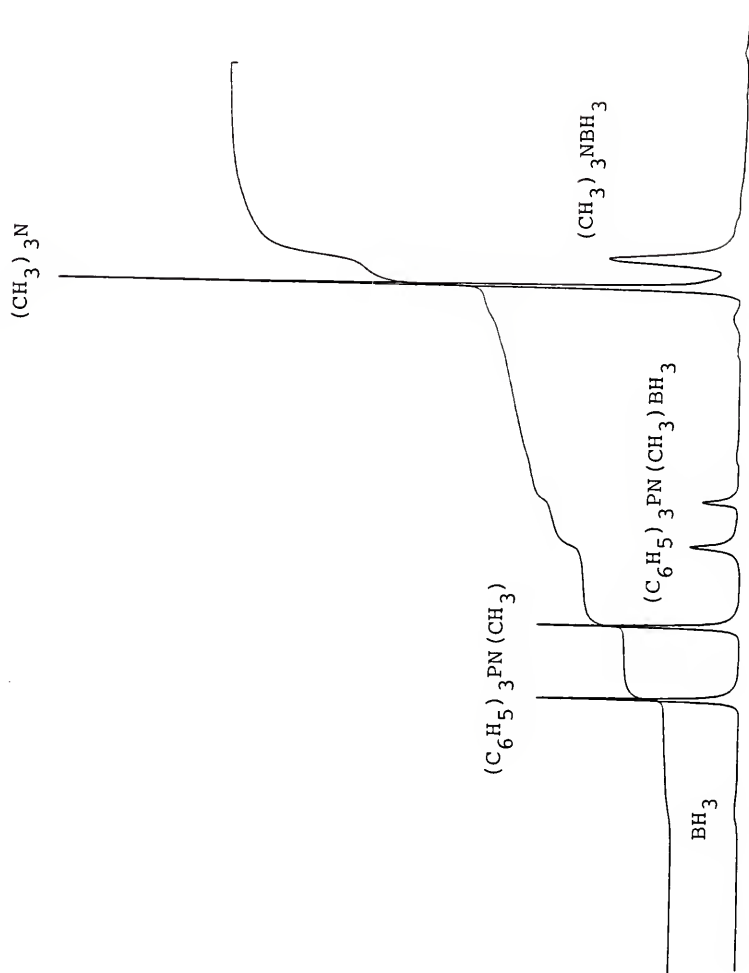


Figure 29. Expansion of ^1H nmr spectrum for exchange of BH_3 between N-methylimino-triphenylphosphorane and trimethylamine borane at 50° .

to arrive at the relative concentrations of these species as reported in Table 20.

The methyl resonances of trimethylamine and trimethylamine borane overlap. Therefore, the relative concentration of the phosphorane borane was substituted for the concentration of trimethylamine. These two concentrations should be the same according to equation (6.1). Since there are nine protons on a trimethylamine group, nine times the relative concentration of the phosphorane borane plus the area under the BH_3 peak were subtracted from the total area under the overlapping trimethylamine and trimethylamine borane peaks. This corrected value was then divided by nine to arrive at the relative concentrations of trimethylamine borane reported in Table 20.

Data Manipulation in the Exchange of BH_3 Between N-Methyliminotriphenylphosphorane and 4-Methylpyridine Borane

Equilibrium constants at 25° and 50° were measured using integrated areas of peaks in the H^1 nmr spectra. Each spectrum was split into half to improve the quality of the integrations. Expansions of the integrated peaks in the 50° determination are presented in Figures 30 and 31 as representative of data treatment for this system. The integrated areas under the peaks were used directly as the relative concentrations of the species. The integral scales in the two expansions are not the same but, since each expansion contains a reactant and a product peak, the scale factors cancel in the equilibrium constant calculation.

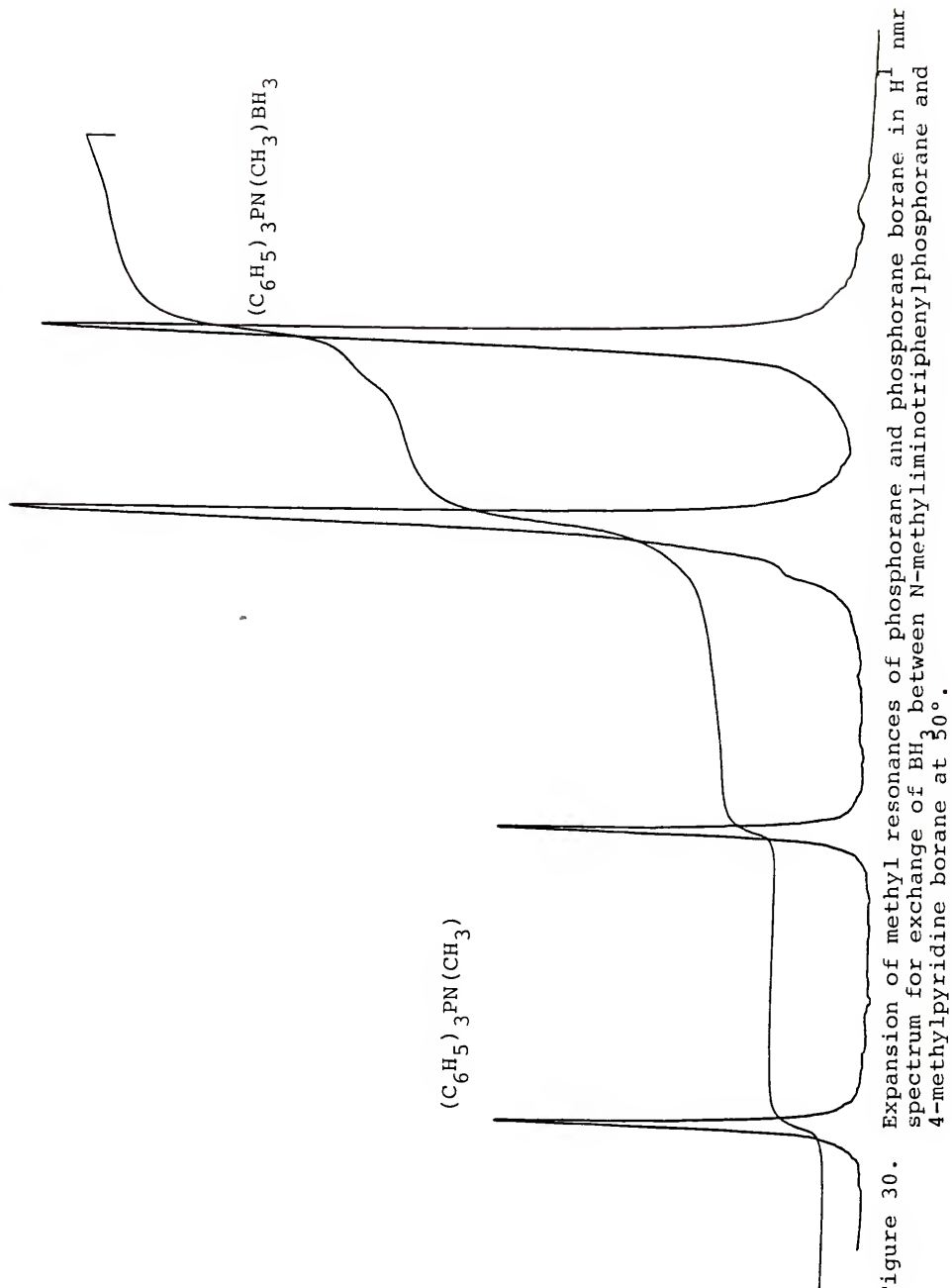


Figure 30. Expansion of methyl resonances of phosphorane and phosphorane borane in ^1H nmr spectrum for exchange of BH_3 between N-methyliminotriphenylphosphorane and 4-methylpyridine borane at 50° .

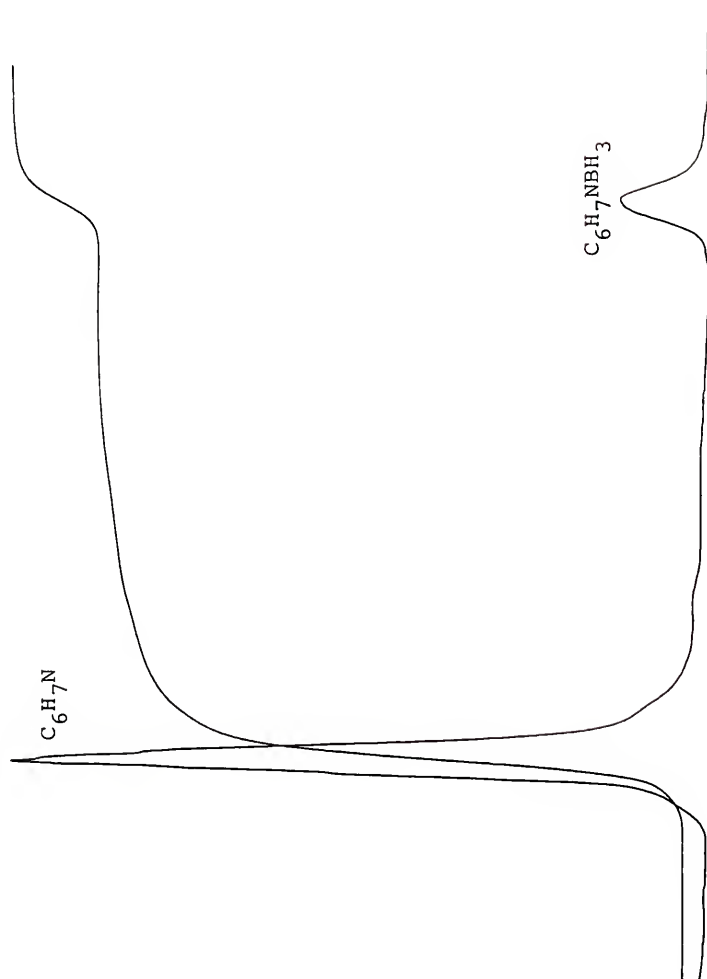


Figure 31. Expansion of methyl resonances of 4-methylpyridine borane and 4-methylpyridine in H^1 nmr spectrum for exchange of BH_3 between N-methyliminotriphenylphosphorane and 4-methylpyridine borane at 50° .

Data Manipulation in the Exchange of BH_3 Between N-n-Propyliminotriphenylphosphorane and 4-Methylpyridine Borane

The equilibrium constant at 50° was measured using integrated areas of peaks in the H^1 nmr spectrum recorded at 300 MHz. An expansion of the integrated peaks of interest is presented in Figure 32. The integrated areas under the 4-methylpyridine borane and 4-methylpyridine peaks were used directly as the relative concentrations of these species. Examination of the expansion reveals that two broad humps overlap with the methyl resonances of the n-propyl groups on the phosphorane and phosphorane borane centered at 1.183 ppm and 0.733 ppm respectively. The humps were assumed to be parts of the proton resonances of the BH_3 groups, although the possibility of them being an unidentified impurity is not excluded. Because of the size and extent of overlap of the hump with the phosphorane borane triplet, the relative concentration of 4-methylpyridine was used as the relative concentration of the phosphorane borane. These two species should be equal in concentration. To correct the integration of the phosphorane triplet, only the area of the parts of the triplet not overlapped by the broad hump was used. This area corresponds to the peaks at 1.183 ppm and 1.159 ppm. Since the triplet has intensities corresponding to 1:2:1, the selected area from the triplet was multiplied by 4/3 to arrive at the relative concentration of N-n-propyliminotriphenylphosphorane.

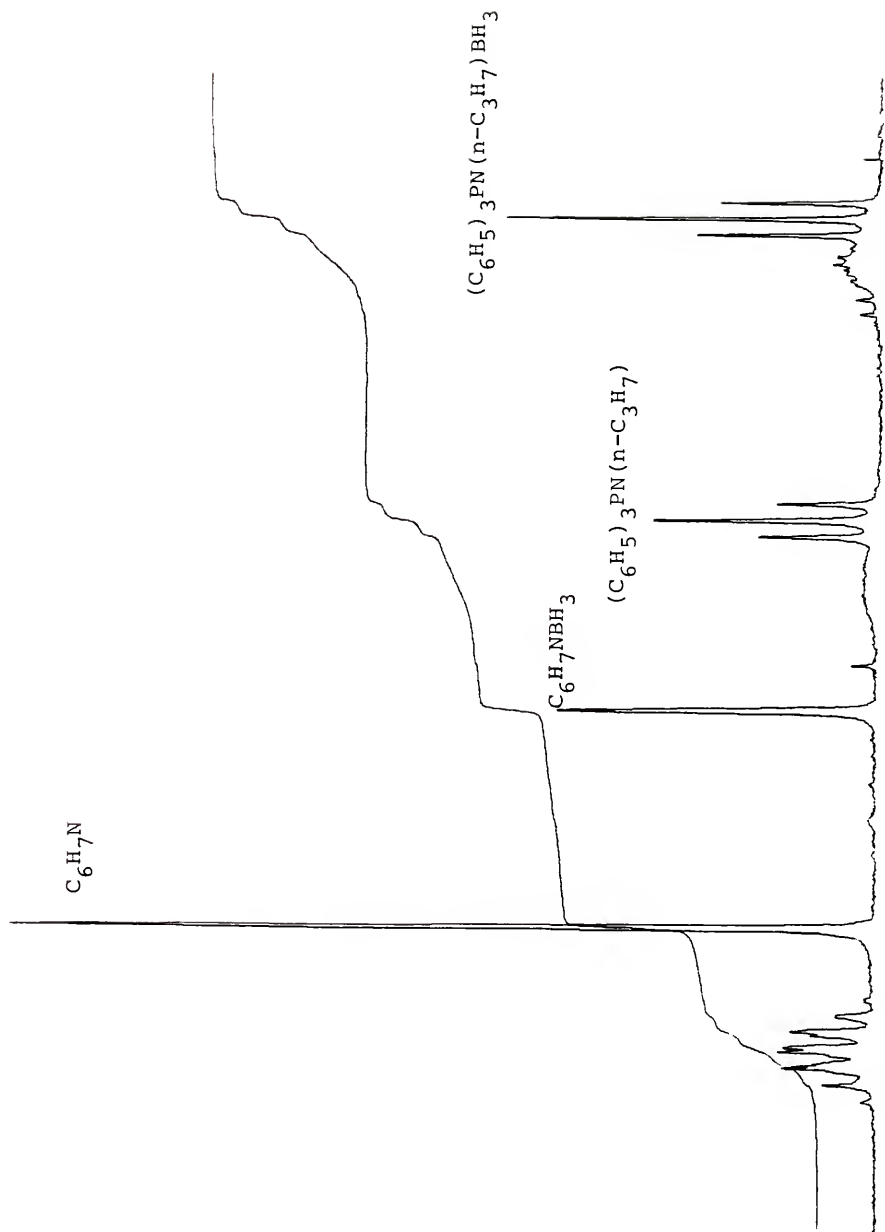


Figure 32. Expansion of ^1H nmr spectrum for exchange of BH_3 between N-n-propylimino-triphenylphosphorane and 4-methylpyridine borane.

Data Manipulation in the Systems Measured by Combinations of
Proton Decoupled P^{31} and B^{11} nmr Spectra

Equilibrium constants at 25° and 50° were measured using integrated areas of peaks in proton decoupled P^{31} and B^{11} nmr spectra. Since neither trimethylamine nor 4-methylpyridine contain either phosphorus or boron, direct measurements of the concentrations of these species were not attained. Instead, an assumption was made that the concentration of the phosphorane borane should be equal to the trimethylamine or 4-methylpyridine concentrations. Therefore, only the relative concentrations of the phosphorane borane were used in the numerator when solving for the equilibrium constants. The equation used to solve for these values is as follows

$$K = \frac{[(C_6H_5)_3PNRBH_3]_B [(C_6H_5)_3PNRBH_3]_P}{[ABH_3]_B [(C_6H_5)_3PNR]_P} \quad (6.3)$$

where B and P denote the nuclei integrated to obtain the respective relative concentrations.

The integrals obtained from the two different spectra have different scales. Since each spectrum contains peaks corresponding to products and reactants, the scaling factors cancel. An integrated P^{31} spectrum corresponding to the exchange of BH_3 between N-ethyliminotriphenylphosphorane and 4-methylpyridine borane at 25° is reproduced in Figure 33. An integrated B^{11} spectrum corresponding to exchange of BH_3

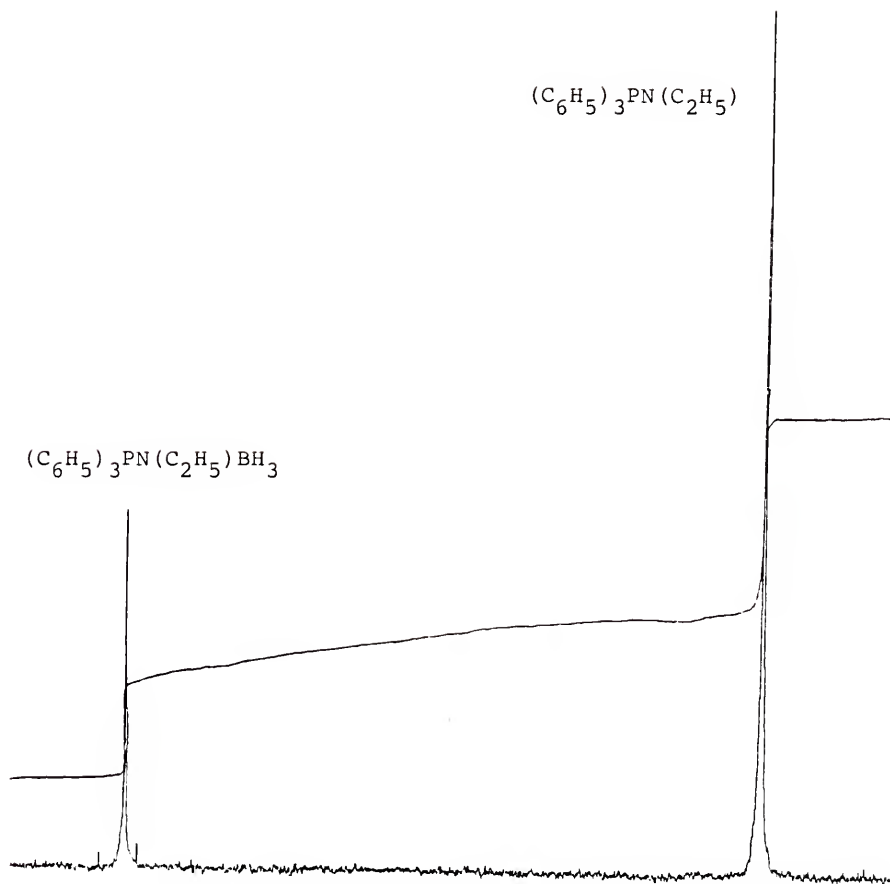


Figure 33. P^{31} nmr spectrum for exchange of BH_3 between N-ethyliminotriphenylphosphorane and 4-methylpyridine borane at 25° .

between N-n-propyliminotriphenylphosphorane and trimethylamine borane at 50° is reproduced in Figure 34.

The equilibrium constants calculated from the data of Tables 19 and 20 are presented in Tables 21 and 22.

Equilibrium Attainment

In order to establish that the two sets of equilibrium constants were consistent, a separate exchange experiment was set up using trimethylamine borane and 4-methylpyridine. An nmr tube was prepared in the general manner previously described. The approximate starting concentrations of the reactants were 0.115 M and 0.102 M in trimethylamine borane and 4-methylpyridine respectively. The tube was kept at 25° for 8 days. A H^1 nmr spectrum was recorded and showed four peaks corresponding to trimethylamine, trimethylamine borane, 4-methylpyridine and 4-methylpyridine borane. The areas under the peaks were integrated. The tube was kept at 25° for an additional 12 days. A H^1 nmr spectrum recorded after this time was identical to that recorded after 8 days. Therefore, equilibrium was attained. The tube was kept at 50° for 9 days. A H^1 nmr spectrum was recorded, and the areas under the peaks were again integrated. The tube was kept at 50° for an additional 6 days. A H^1 nmr spectrum recorded after this time was identical to that recorded after 9 days. Thus, equilibrium was attained at 50°. Data from this experiment are presented in Table 23.

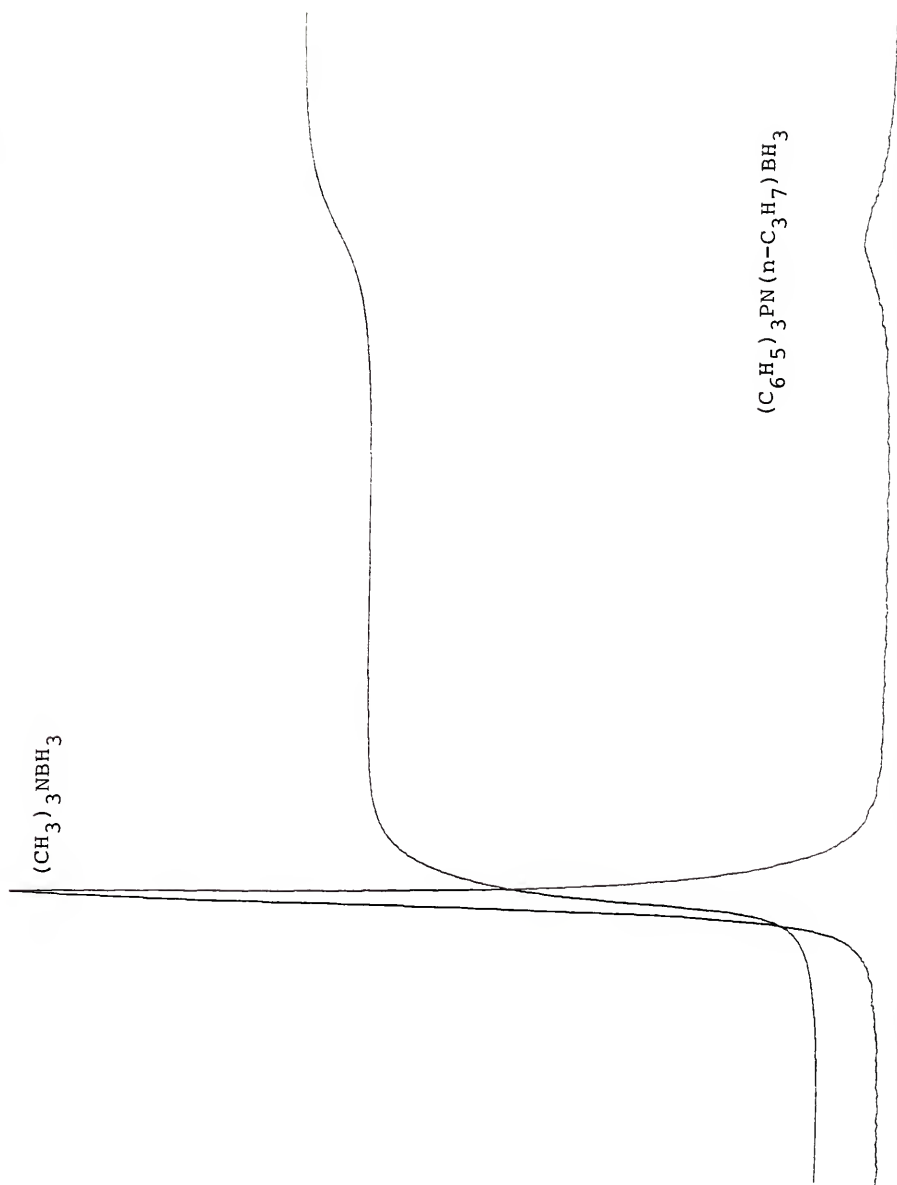
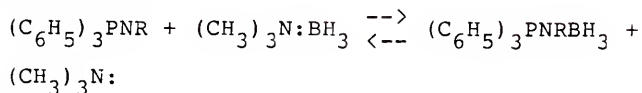


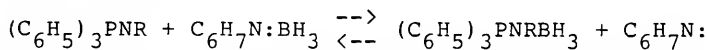
Figure 34. Proton decoupled ^{11}B nmr spectrum for exchange of BH_3 between N-n-propylimino-triphenylphosphorane and trimethylamine borane at 50° .

Table 21. Equilibrium Constants for Exchange of BH_3
According to



Alkyl Group	Temperature °C	K_T
Methyl	25	5.47×10^{-2}
Methyl	50	8.08×10^{-1}
Ethyl	25	1.46×10^{-3}
Ethyl	50	1.51×10^{-1}
n-Propyl	50	5.00×10^{-2}
Isopropyl	50	5.6×10^{-3}
Isobutyl	50	1.6×10^{-2}

Table 22. Equilibrium Constants for Exchange of BH_3
According to



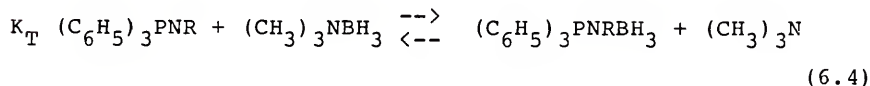
Alkyl Group	Temperature °C	K_P
Methyl	25	4.20
Methyl	50	32.7
Ethyl	25	1.04×10^{-1}
Ethyl	50	6.02
n-Propyl	50	2.03
Isopropyl	50	2.24×10^{-1}
Isobutyl	50	6.82×10^{-1}

Table 23. ^1H NMR Data for Exchange of BH_3 According to
 $\text{C}_6\text{H}_7\text{N:} + (\text{CH}_3)_3\text{N:} \xrightarrow{\text{C}_6\text{H}_7\text{N:} + (\text{CH}_3)_3\text{N:}} \text{C}_6\text{H}_7\text{N:} + (\text{CH}_3)_3\text{N:}$

Temperature °C	Time Days	Relative Concentrations mm				K_{TP}
		4-Picoline Borane	4-Picoline Trimethylamine Borane	Trimethylamine		
25	8	18.3	1.4	7.86	1.4	1.4×10^{-2}
50	9	18.2	1.9	8.17	1.9	2.4×10^{-2}

Because of overlapping peaks, some data manipulation was necessary. An expansion of the integrated peaks of interest is reproduced in Figure 35, corresponding to 25°, as representative of the proton spectra used in this experiment. The areas under the 4-methylpyridine and 4-methylpyridine borane peaks were each divided by three to obtain the relative concentrations of these components. Since the trimethylamine and trimethylamine borane peaks overlap, the relative concentration of 4-methylpyridine borane was used as the relative concentration of trimethylamine. Nine times the relative concentration of trimethylamine was subtracted from the total area of the overlapping trimethylamine, trimethylamine borane peaks. This corrected area was then divided by 9.608 to arrive at the relative concentration of trimethylamine borane. The value 9.608 was used because the trimethylamine borane peak corresponds to nine protons plus 3/4 of a proton, from the BH₃ group of trimethylamine borane, which occurs under the resonance.

To determine that equilibrium had occurred in the phosphorane experiments, equilibrium constants for the exchange of BH₃ between trimethylamine borane and 4-methylpyridine were calculated as follows.



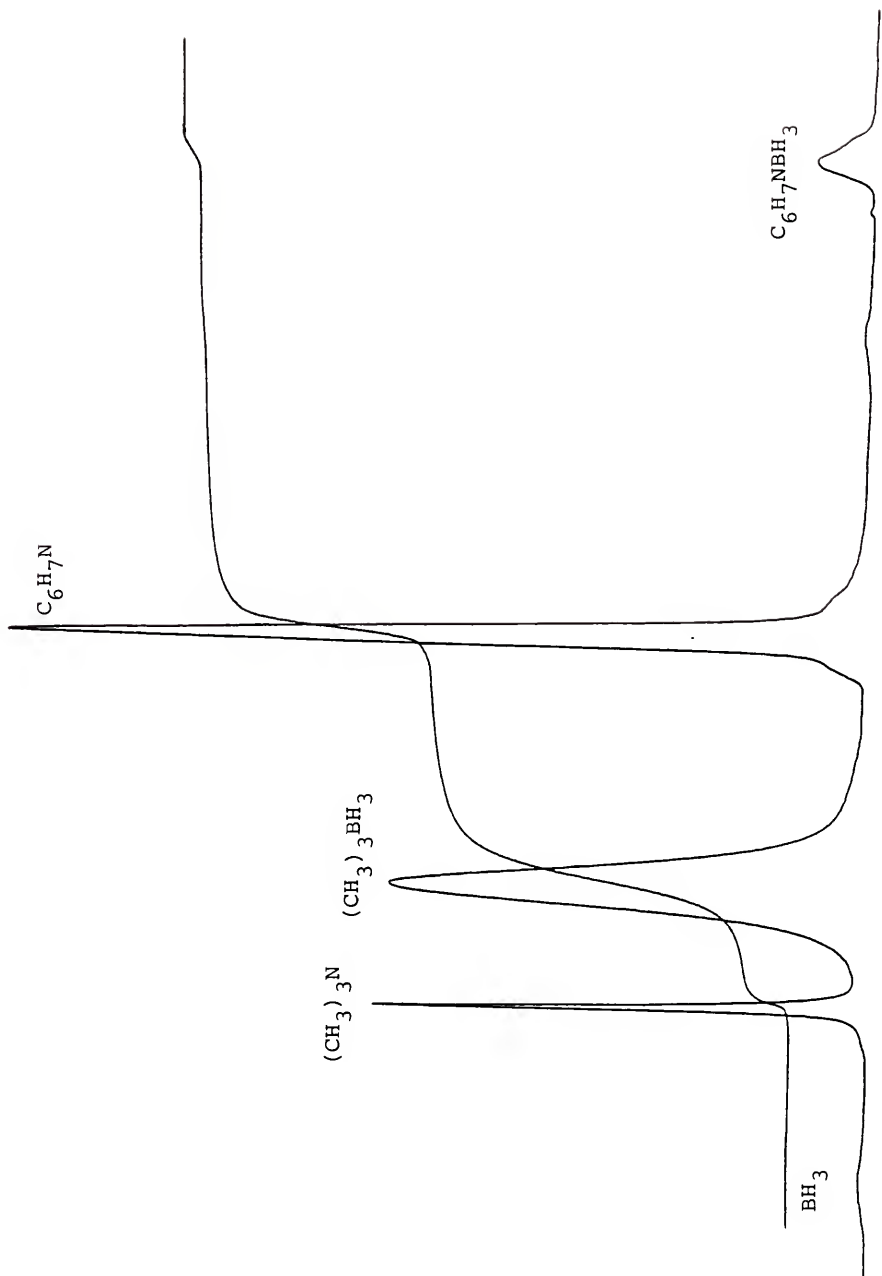
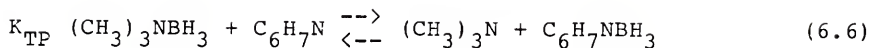
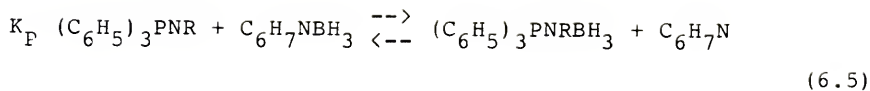


Figure 35. Expansion of H^1 spectrum for exchange of BH_3 between 4-methylpyridine and trimethylamine borane at 25°.



$$(6.4) - (6.5) = (6.6) \quad K_{TP} = \frac{K_T}{K_P} \quad (6.7)$$

Calculated values of K_{TP} using equation (6.7) are presented in Table 24 along with the % differences from the experimentally determined values.

Discussion and Errors

In general, it was found that BH_3 exchanges between trimethylamine borane and N-alkyliminotriphenylphosphanes and between 4-methylpyridine borane and N-alkyliminotriphenylphosphanes in those cases where alkyl equals methyl, ethyl, n-propyl, isopropyl and isobutyl. In those experiments where alkyl equals tert-butyl, no exchange of BH_3 was observed. Two other experiments were performed to determine whether this was a consequence of slow kinetics or unfavorable thermodynamics.

Two nmr tubes were prepared in the general manner previously described. The approximate starting concentrations of the reactants in the first tube were 0.0146 M and 0.0130 M in trimethylamine and N-tert-butyliminotriphenylphosphorane borane respectively. The approximate

Table 24. Calculated Values of K_{TP} Using Equation (6.7).

Alkyl Group	Temperature °C	K_{TP}	% Difference
Methyl	25	1.30×10^{-2}	4.7%
Methyl	50	2.47×10^{-2}	3.1%
Ethyl	25	1.4×10^{-2}	2.8%
Ethyl	50	2.5×10^{-2}	4.9%
n-Propyl	50	2.46×10^{-2}	2.5%
Isopropyl	50	2.5×10^{-2}	4.9%
Isobutyl	50	2.3×10^{-2}	4.3%

starting concentrations of the reactants in the second tube were 0.0154 M and 0.0142 M in 4-methylpyridine and N-tert-butyliminotriphenylphosphorane borane respectively. The low concentrations are a result of the limited solubility of the borane in benzene. The tubes were kept at 25° for 10 days. Phosphorus-31 nmr spectra recorded after this time showed only one peak corresponding to N-tert-butyliminotriphenylphosphorane borane in each tube. The tubes were then kept at 50° for 7 days. Phosphorus-31 nmr spectra recorded after this time showed only one peak corresponding to N-tert-butyliminotriphenylphosphorane for each tube. Therefore, all of the BH_3 was transferred to the trimethylamine or 4-methylpyridine molecules at that temperature.

Throughout the calculations performed in this chapter, rounding off of numbers was not done until the final calculations to reduce error propagation.

In general, the equilibrium constants for exchange were measured by integrating areas under peaks in proton decoupled P^{31} and B^{11} nmr spectra and in H^1 nmr spectra. Proton nmr could only be used in those cases where overlapping of peaks did not cause a problem. All of the values for K_{TP} calculated by equation (6.7) are within five percent of the directly determined experimental values. Therefore, all of the experiments had reached equilibrium.

Exchange occurred at 25° in those experiments in which the alkyl groups were methyl and ethyl. Exchange occurred at 50° in all the experiments except when alkyl equaled tert-butyl.

In general, the exchange reactions were found to be slow kinetically to come to equilibrium. The times reported in Tables 19 and 20 represent the times which had elapsed before final equilibrium was measured. They do not necessarily represent the time each experiment took to reach equilibrium. In a few instances the reaction kinetics were followed. It was observed that in the exchange reactions where the alkyl group was methyl, that 41 and 70 days were required at 25° for equilibrium to be attained with trimethylamine borane and 4-methylpyridine borane respectively. In all the instances where the kinetics of the exchange

reactions were followed, trimethylamine borane reached equilibrium sooner than 4-methylpyridine borane.

Two mechanisms for exchange of BH_3 are possible. The first to be discussed is $\text{Sn}1$. If a $\text{Sn}1$ mechanism occurs, the activation energy would be the heterolytic B-N bond energy. Since trimethylamine is a stronger base than 4-methylpyridine, the activation energy for exchange with trimethylamine borane would be higher than with 4-methylpyridine borane. One would predict that in a $\text{Sn}1$ mechanism, trimethylamine borane would exchange BH_3 slower than 4-methylpyridine borane. This prediction contradicts the observed reaction kinetics. Therefore, a $\text{Sn}1$ mechanism cannot occur.

The other alternative is a $\text{Sn}2$ mechanism. Assuming a $\text{Sn}2$ mechanism occurs, the difference in reactivity of the borane adducts can be explained by steric factors. Trimethylamine is a bulkier base than 4-methylpyridine. Although trimethylamine is a stronger base than 4-methylpyridine, the transition state in the displacement of trimethylamine should be lower in energy than with 4-methylpyridine. More energy would be released from relief of the steric strain in the trimethylamine displacement than in the 4-methylpyridine displacement. Therefore, trimethylamine borane would exchange BH_3 faster than 4-methylpyridine borane.

Using the equilibrium constants as a measurement of relative Lewis base strengths, it was found that all of the

N-alkyliminotriphenylphosphoranes are weaker bases than trimethylamine. It was observed that N-methyliminotriphenylphosphorane is a stronger base than 4-methylpyridine. Also, N-ethyl and N-n-propyliminotriphenylphosphoranes were found to be stronger bases than 4-methylpyridine at 50°. In those cases where the alkyl groups were isopropyl, isobutyl and tert-butyl, 4-methylpyridine is the stronger base.

In general, as the alkyl group becomes larger, the basicity of the corresponding phosphorane decreases. This is most pronounced for the branched-chain alkyl groups. The same type of observation was made by Zimmer and Singh (26) in studies of BF_3 addition compounds of N-alkyliminotriphenylphosphoranes. Two different explanations can be given to describe this phenomenon. The first explanation employs front strain. The bulkier alkyl groups repel the BH_3 unit and thus shield the basic lone pairs. The second explanation uses back strain. The bulky phenyl rings on the phosphorus atom repel the alkyl groups by differing amounts according to their steric bulk. This should cause the P-N-C bond angle to increase approaching a maximum of 180°. As this angle becomes larger, the orbital containing the lone pair on nitrogen can overlap better with an empty d orbital on phosphorus, increasing the multiple bonding and decreasing the basicity.

It would be reasonable on σ considerations to predict that the N-alkyliminotriphenylphosphoranes would show an increase in basicity as the alkyl group size increases. It

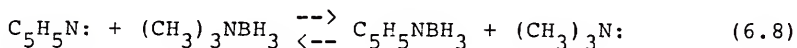
was observed, however, in Chapter VII that a substantial decrease in π bonding occurs upon coordination of the phosphoranes by BH_3 . The decrease in π bonding varies considerably. Therefore, when interpreting base strengths of the N-alkyliminotriphenylphosphoranes, the total interaction energy in the molecule must be considered since a decrease in π bonding between phosphorus and nitrogen would raise the energy of the molecule. The loss in π overlap is greater the larger the alkyl group. Therefore one cannot make easy predictions about the base strengths of these compounds.

The change in π bonding can also be used to explain the general slowness of the exchange reactions. As the phosphorane approaches the borane adduct in a $\text{S}_\text{N}2$ mechanism, a partial bond is formed between the phosphorane nitrogen lone pair and the boron 2p orbital. An increase in bonding between the phosphorane and BH_3 would decrease π bonding between phosphorus and nitrogen. Therefore, the total energy of the transition state would be increased by the loss in π bonding, and the reaction rate would decrease.

The equilibrium constants are larger for exchange between 4-methylpyridine borane than between trimethylamine borane for a given alkyl group. Indeed, a separate experiment of exchange of BH_3 between trimethylamine borane and 4-methylpyridine at 25° and 50° shows that trimethylamine is a much stronger base than 4-methylpyridine. This observation corresponds well with the basic dissociation constants

(75) of 7.4×10^{-5} and 1.1×10^{-8} for trimethylamine and 4-methylpyridine respectively.

Brown et al. (11) found that when trimethylamine and pyridine borane were allowed to react in the gas phase, the system comes to equilibrium rapidly, and the equilibrium point lies toward the formation of trimethylamine borane (85:15). The equilibrium constant for equation (6.8) would therefore be $K_{eq} = 3.1 \times 10^{-2}$.

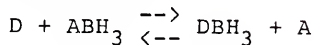


This value is on the same order of magnitude as K_{TP} . Therefore, the equilibrium constants observed in the present study correlate well with work done by previous investigators in this field.

In those exchange experiments where equilibrium constants were obtained at two different temperatures, enthalpies of reaction were calculated using the Clausius-Clapeyron equation. Entropies of reaction were also calculated using the calculated enthalpies. The values for ΔH and ΔS of the specific reactions are presented in Table 25.

One would assume that the enthalpies of the reactions correspond to differences in the B-N heterolytic bond energies. This assumption is valid for the reaction between trimethylamine borane and 4-methylpyridine. The ΔH value in this example of 4.13 kcal/mole is a reasonable difference in the B-N heterolytic bond energies. The entropy change for

Table 25. Enthalpies and Entropies of Reaction for Exchange of BH_3 According to



D	A	ΔH kcal/mole	ΔS cal/mole $^\circ\text{K}$
$(\text{C}_6\text{H}_5)_3\text{PNCH}_3$	$(\text{CH}_3)_3\text{N}$	20.6	63.3
$(\text{C}_6\text{H}_5)_3\text{PNCH}_3$	$\text{C}_6\text{H}_7\text{N}$	15.7	55.5
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{C}_2\text{H}_5)$	$(\text{CH}_3)_3\text{N}$	35.5	106
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{C}_2\text{H}_5)$	$\text{C}_6\text{H}_7\text{N}$	31.0	99.7
$\text{C}_6\text{H}_7\text{N}$	$(\text{CH}_3)_3\text{N}$	4.13	5.4

the reaction of 5.4 cal/mole $^\circ\text{K}$ is also a reasonable number and could reflect the difference in order of the solvent molecules around products and reactants. The enthalpies of reaction involving BH_3 exchange with the phosphoranes are larger in magnitude than the value in the amine reaction. The numbers are too large to represent only the difference between the B-N heterolytic bond energies.

One can explain the large magnitude of these numbers through changes in the π bonding between phosphorus and nitrogen. It was observed in Chapter VII that π bonding decreases upon coordination of the phosphoranes by BH_3 . The decrease in π bonding would increase the energy of the

corresponding borane adduct. The increase in energy would be reflected in the enthalpy of the reaction. Claydon, Fowell and Mortimer (47) estimated that 58 kcal/mole of energy is attributable to the π bonding system of electrons in N-ethyliminotriphenylphosphorane. With this value in mind, the ΔH values for the phosphoranes seem reasonable, and the majority of the energy change can be attributable to the decrease in π bonding between phosphorus and nitrogen. Data in Chapter VII show that the change in π bonding of N-ethyliminotriphenylphosphorane upon coordination by BH_3 is larger in magnitude than that seen when N-methyliminotriphenylphosphorane is coordinated by BH_3 . Thus, the larger reaction enthalpies in the N-ethyliminotriphenylphosphorane examples are consistent with the notion of change in π bonding.

The large positive entropies of reaction in the phosphorane examples indicate that the corresponding exchange reactions are probably driven by entropy since ΔH is positive. Since phosphoranes and their corresponding borane adducts are structurally similar, the entropy changes cannot be explained through increases in translational degrees of freedom. The values must therefore correspond to changes in rotational and vibrational degrees of freedom. It is quite reasonable to expect a decrease in the rotational barrier around the P-N bond with a decrease in π bonding. One would also expect the force constants for P-N vibrations to decrease with a decrease in π bonding. This decrease in

force constant is reflected in the observed shifts toward lower wavenumbers of the P-N vibrations in the infrared spectra upon coordination by BH_3 .

The thermodynamic data derived from equilibrium constants for exchange of BH_3 must therefore be interpreted in light of the total energy changes of the molecules and cannot represent only the change in B-N heterolytic bond energies.

The equilibrium constants measured in the present study are subject to error due to the manner in which they were obtained. All of the experiments were probed by modern pulsed FT-NMR techniques. Pulsed nmr operates by irradiation of lower energy state nuclei by a broad band of rf frequency to promote everything to the higher energy state. After each pulse, the promoted nuclei return back to the ground state releasing energy which is measured by the detector. If all of the promoted nuclei do not return to the ground state before the next pulse, saturation will occur, and an error in peak areas will result.

All of the proton spectra contained unresolved resonances from the boron attached protons. Some corrections could be performed in the trimethylamine experiments because the quadrupole broadening was not too great. The other BH_3 protons could not be corrected for, however, because these peaks were too broad to be located. The peaks would still show up in the integrated areas, and some error can be expected in the equilibrium constants in these cases.

In some of the boron spectra, the broad resonances overlapped slightly. No attempt was made to correct for this problem, and therefore errors in the equilibrium constants are expected.

CHAPTER VII
DETERMINATION OF THE AMOUNT OF PI-BONDING
BETWEEN PHOSPHORUS AND NITROGEN

Bonding between phosphorus and nitrogen in N-substituted-iminotriphenylphosphoranes and their derivatives has generally been considered as a combination of σ and π bonding. The σ bond is formed from a sp^3 orbital on phosphorus and a sp^2 orbital on nitrogen. The π bonds can be formed by overlap of empty 3d orbitals on phosphorus with a filled 2p orbital and with the sp^2 lone pair on nitrogen. In order to determine the amount of overlap in the π system, two separate physical properties, bond lengths and P^{31} nmr chemical shifts, were studied employing N-substituted-iminotriphenylphosphoranes and their derivatives.

Pi-Bond Character Measured from Phosphorus-
Nitrogen Bond Distances

Bond lengths have been used in numerous chemical compounds to determine the presence of multiple bonding between atoms. Bond lengths significantly smaller than the sum of covalent radii imply that some degree of multiple bonding must be present. In order to determine the effects of complexation of the sp^2 lone pair and charge formation on

the degree of π bonding between phosphorus and nitrogen, crystal structures of two structurally similar compounds were determined. The compounds chosen were the iso-electronic species N-methyliminotriphenylphosphorane borane and N,N-dimethylaminotriphenylphosphonium ion as the tetrafluoroborate salt.

Crystal Structure of N-Methyliminotriphenylphosphorane Borane

Single crystals suitable for a X-ray diffraction study were obtained by slow recrystallization from a benzene solution. The structure was determined on a Nicolet R3M diffractometer using Mo-K α radiation. The space group was determined to be P 2₁/N. The structure of the molecule is reproduced in Figure 36. Bond lengths and bond angles are presented in Tables 26 and 27 respectively.

Crystal Structure of N,N-Dimethylaminotriphenylphosphonium Tetrafluoroborate

The compound N,N-dimethylaminotriphenylphosphonium tetrafluoroborate was prepared by the following procedure.

To N,N-dimethylaminotriphenylphosphonium iodide, 0.443 g (1.02 mmoles), in 75 ml of deionized water, a solution of 48% tetrafluoroboric acid, 5 ml (27.3 mmoles of HBF₄), was added. A yellow-white precipitate formed immediately. The product was filtered and washed with two portions of 10 ml each of ice cold deionized water. The solid was then washed with three portions of 20 ml each of

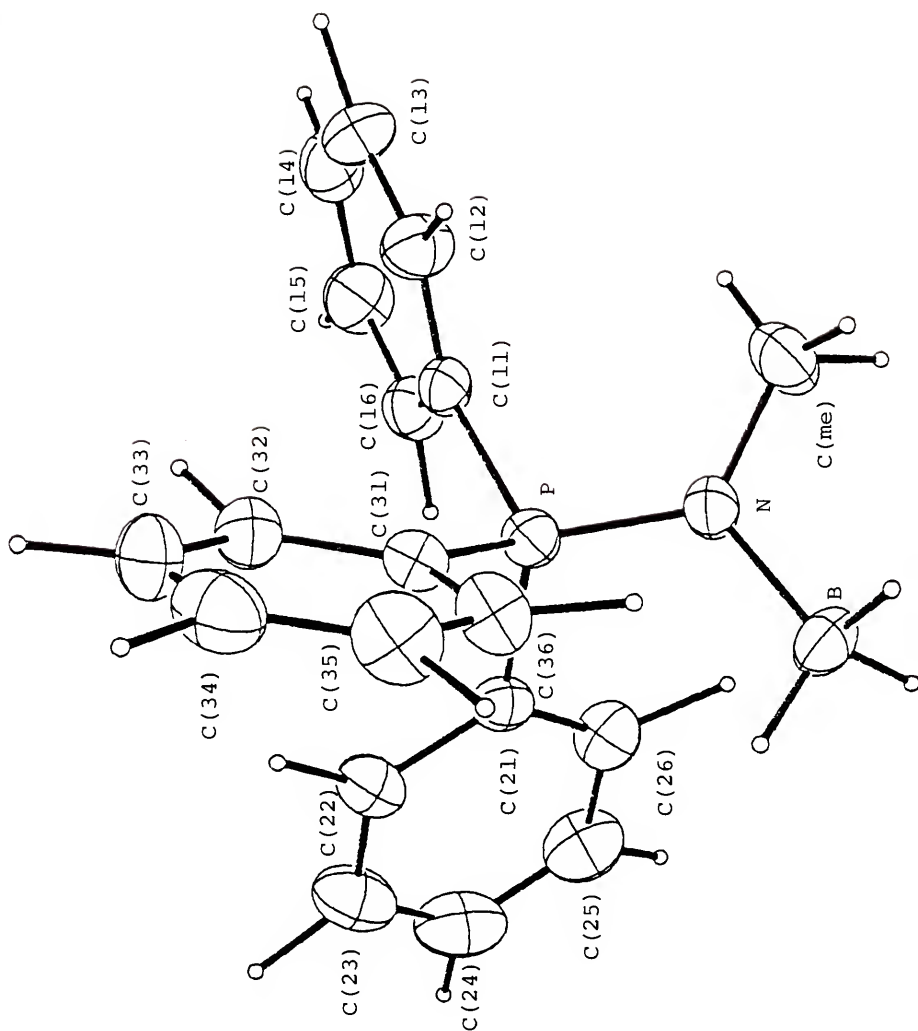


Figure 36. Structure of N-methyliminotriphenylphosphorane borane.

Table 26. Bond Lengths in N-Methyliminotriphenylphosphorane Borane.

Bond	Bond Length, Å, with Standard Deviation in Parentheses
P-N	1.605 (3)
P-C (11)	1.803 (3)
P-C (21)	1.804 (4)
P-C (31)	1.808 (3)
N-C (Me) *	1.456 (5)
N-B	1.583 (5)
C (11) - C (12)	1.389 (5)
C (12) - C (13)	1.398 (5)
C (13) - C (14)	1.378 (6)
C (14) - C (15)	1.383 (6)
C (15) - C (16)	1.402 (5)
C (11) - C (16)	1.389 (5)
C (21) - C (22)	1.395 (5)
C (22) - C (23)	1.397 (5)
C (23) - C (24)	1.377 (6)
C (24) - C (25)	1.390 (6)
C (25) - C (26)	1.397 (6)
C (21) - C (26)	1.386 (5)
C (31) - C (32)	1.401 (5)
C (32) - C (33)	1.404 (5)
C (33) - C (34)	1.372 (6)
C (34) - C (35)	1.374 (6)
C (35) - C (36)	1.398 (6)
C (31) - C (36)	1.382 (5)

* Me = methyl

Table 27. Bond Angles in N-Methyliminotriphenylphosphorane Borane.

Bonds	Bond Angle ($^{\circ}$), with Standard Deviation in Parentheses
P-N-B	120.7 (2)
P-N-C (Me) *	124.3 (2)
C (Me) -N-B	114.6 (3)
N-P-C (11)	110.9 (2)
N-P-C (21)	110.6 (2)
N-P-C (31)	114.6 (2)
C (11) -P-C (21)	106.7 (2)
C (21) -P-C (31)	107.5 (2)
C (11) -P-C (31)	106.2 (2)
P-C (11) -C (12)	119.3 (3)
P-C (11) -C (16)	120.4 (3)
C (11) -C (12) -C (13)	119.5 (4)
C (12) -C (13) -C (14)	120.1 (4)
C (13) -C (14) -C (15)	120.9 (4)
C (14) -C (15) -C (16)	119.4 (4)
C (11) -C (16) -C (15)	119.8 (3)
C (12) -C (11) -C (16)	120.3 (3)
P-C (21) -C (22)	120.8 (3)
P-C (21) -C (26)	117.9 (3)
C (21) -C (22) -C (23)	118.4 (3)
C (22) -C (23) -C (24)	120.9 (4)
C (23) -C (24) -C (25)	120.2 (4)
C (24) -C (25) -C (26)	119.9 (4)
C (21) -C (26) -C (25)	119.4 (4)
C (22) -C (21) -C (26)	121.2 (3)
P-C (31) -C (32)	120.8 (3)
P-C (31) -C (36)	118.8 (3)
C (31) -C (32) -C (33)	118.5 (3)

Continued

Table 27. Continued.

Bonds	Bond Angle ($^{\circ}$), with Standard Deviation in Parentheses
<hr/>	
C(32)-C(33)-C(34)	120.9(4)
C(33)-C(34)-C(35)	120.1(4)
C(34)-C(35)-C(36)	120.3(4)
C(31)-C(36)-C(35)	119.8(4)
C(32)-C(31)-C(36)	120.3(3)

*
Me = methyl

diethyl ether and was dried in vacuo. The crude product weighed 0.323 g (80% yield), mp 152-155°.

A portion of the product (0.169 g) was recrystallized from a chloroform-ethyl acetate solvent mixture to produce white needles suitable for a X-ray diffraction study. The recovered material (0.119 g, 70% yield) melted at 155-156°. The analysis of the recrystallized material was %C 60.70, %H 5.47, %N 3.44, calculated: %C 61.10, %H 5.38, %N 3.56.

The structure was determined on a Syntex P1 diffractometer using Cu-K α radiation with a nickel filter. The space group was determined to be P 2₁/C. Two different structures were found in the lattice. These are reproduced in Figures 37 and 38. Structures for the tetrafluoroborate anions are reproduced in Figure 39. Bond lengths and bond angles are presented in Tables 28 and 29 respectively.

Discussion of Crystal Data

Analysis of the crystal data reveals that the boron, nitrogen, methyl carbon and phosphorus atoms of the borane adduct are coplanar. Also, the methyl carbon, nitrogen and phosphorus atoms of each phosphonium cation are essentially coplanar. These observations imply sp² hybridization of the nitrogen atoms as expected. Planes in the borane adduct are defined as follows: plane 1 contains carbon atoms C(11)-C(16); plane 2 contains carbon atoms C(21)-C(26); plane 3 contains carbon atoms C(31)-C(36); plane 4 contains

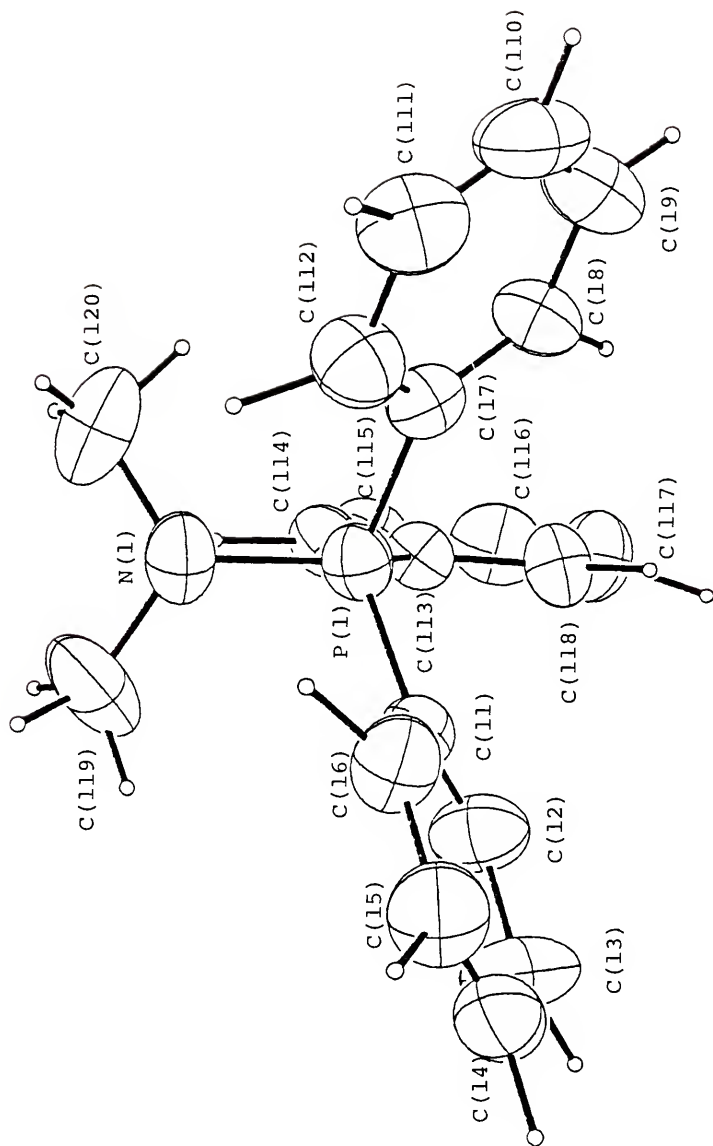


Figure 37. Structure of cation 1 in N,N-dimethylaminotriphenylphosphonium tetrafluoroborate.

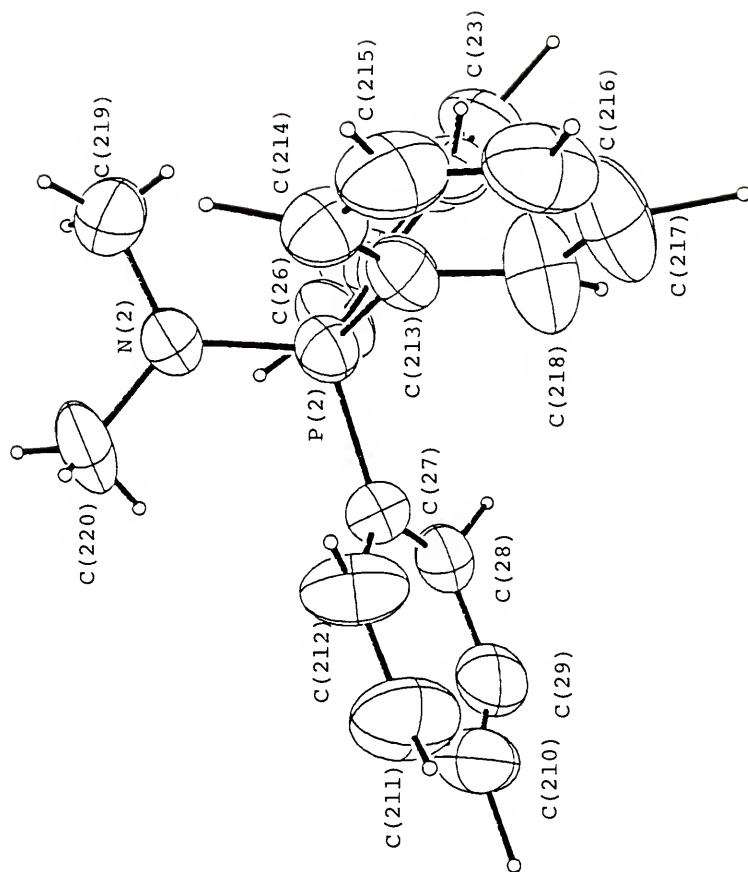


Figure 38. Structure of cation 2 in N,N-dimethylaminotriphenylphosphonium tetrafluoroborate.

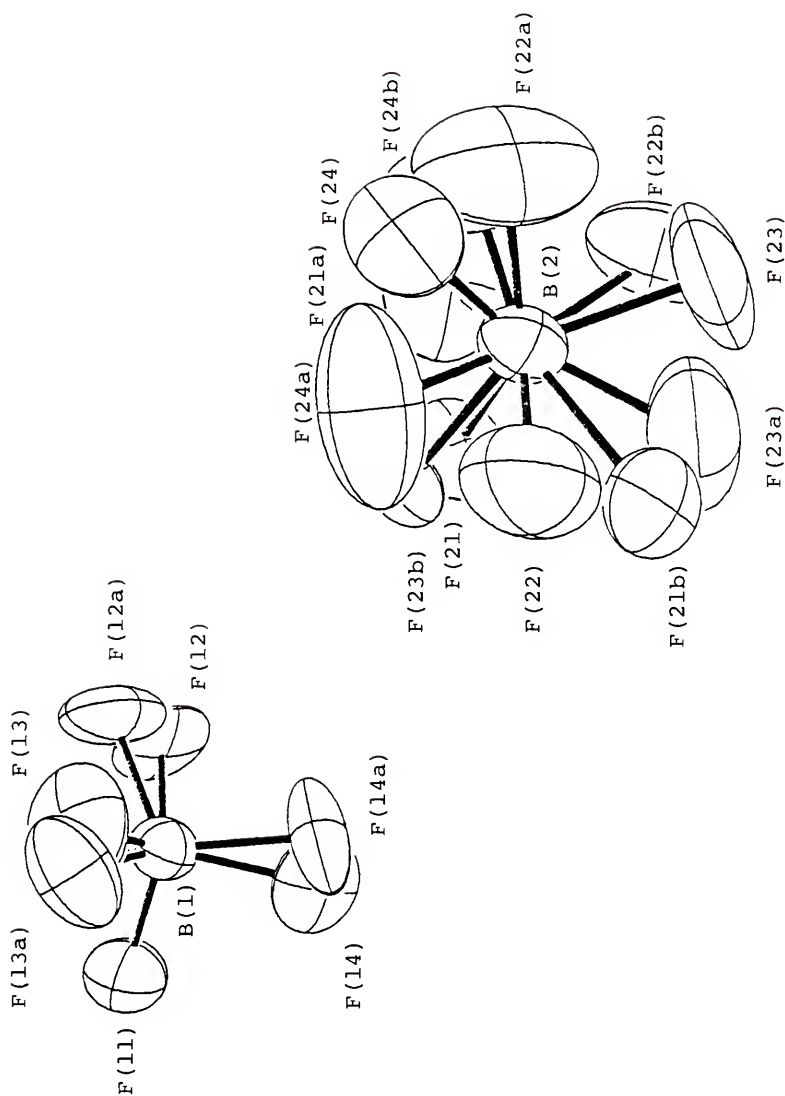


Figure 39. Structures of tetrafluoroborate anions in *N,N*-dimethylamino-triphenylphosphonium tetrafluoroborate.

Table 28. Bond Lengths in N,N-Dimethylaminotriphenylphosphonium Tetrafluoroborate.

Bond	Bond Length, Å, with Standard Deviation in Parentheses
P(1)-N(1)	1.627(4)
P(1)-C(11)	1.796(5)
P(1)-C(17)	1.805(5)
P(1)-C(113)	1.789(5)
N(1)-C(119)	1.443(7)
N(1)-C(120)	1.440(7)
C(11)-C(12)	1.369(7)
C(12)-C(13)	1.391(7)
C(13)-C(14)	1.383(8)
C(14)-C(15)	1.367(8)
C(15)-C(16)	1.396(8)
C(11)-C(16)	1.384(7)
C(17)-C(18)	1.376(7)
C(18)-C(19)	1.379(7)
C(19)-C(110)	1.386(8)
C(110)-C(111)	1.369(8)
C(111)-C(112)	1.395(7)
C(17)-C(112)	1.412(7)
C(113)-C(114)	1.397(6)
C(114)-C(115)	1.378(7)
C(115)-C(116)	1.371(7)
C(116)-C(117)	1.390(7)
C(117)-C(118)	1.406(7)
C(113)-C(118)	1.395(7)
P(2)-N(2)	1.624(4)
P(2)-C(21)	1.788(5)
P(2)-C(27)	1.789(5)
P(2)-C(213)	1.803(5)

Continued

Table 28. Continued.

Bond	Bond Length, Å, with Standard Deviation in Parentheses
N(2)-C(219)	1.461(6)
N(2)-C(220)	1.425(7)
C(21)-C(22)	1.388(7)
C(22)-C(23)	1.377(8)
C(23)-C(24)	1.370(8)
C(24)-C(25)	1.379(8)
C(25)-C(26)	1.386(8)
C(21)-C(26)	1.379(7)
C(27)-C(28)	1.401(7)
C(28)-C(29)	1.407(7)
C(29)-C(210)	1.375(8)
C(210)-C(211)	1.388(8)
C(211)-C(212)	1.398(8)
C(27)-C(212)	1.376(8)
C(213)-C(214)	1.371(7)
C(214)-C(215)	1.375(7)
C(215)-C(216)	1.365(9)
C(216)-C(217)	1.353(10)
C(217)-C(218)	1.406(9)
C(213)-C(218)	1.376(8)
B(1)-F(11)	1.395(7)
B(1)-F(12)	1.246(8)
B(1)-F(12a)	1.415(10)
B(1)-F(13)	1.293(27)
B(1)-F(13a)	1.350(25)
B(1)-F(14)	1.348(9)
B(1)-F(14a)	1.357(9)
B(2)-F(21)	1.375(11)
B(2)-F(21a)	1.412(14)

Continued

Table 28. Continued.

Bond	Bond Length, Å, with Standard Deviation in Parentheses
B(2)-F(21b)	1.535(11)
B(2)-F(22)	1.232(14)
B(2)-F(22a)	1.351(30)
B(2)-F(22b)	1.311(16)
B(2)-F(23)	1.338(17)
B(2)-F(23a)	1.273(17)
B(2)-F(23b)	1.361(11)
B(2)-F(24)	1.301(21)
B(2)-F(24a)	1.334(15)
B(2)-F(24b)	1.168(37)

Table 29. Bond Angles in N,N-Dimethylaminotriphenylphosphonium Tetrafluoroborate.

Bonds	Bond Angle, ($^{\circ}$), with Standard Deviation in Parentheses
P(1)-N(1)-C(119)	122.7(3)
P(1)-N(1)-C(120)	122.6(4)
C(119)-N(1)-C(120)	112.8(8)
C(11)-P(1)-N(1)	107.0(2)
C(17)-P(1)-N(1)	106.7(2)
C(113)-P(1)-N(1)	113.3(2)
C(11)-P(1)-C(17)	111.6(2)
C(11)-P(1)-C(113)	108.4(2)
C(17)-P(1)-C(113)	109.9(2)
P(1)-C(11)-C(12)	120.5(4)
P(1)-C(11)-C(16)	118.8(3)
C(11)-C(12)-C(13)	120.3(5)
C(12)-C(13)-C(14)	119.6(5)
C(13)-C(14)-C(15)	119.8(5)
C(14)-C(15)-C(16)	121.1(5)
C(11)-C(16)-C(15)	118.5(4)
C(12)-C(11)-C(16)	120.7(4)
P(1)-C(17)-C(18)	121.3(4)
P(1)-C(17)-C(112)	117.4(4)
C(17)-C(18)-C(19)	119.3(5)
C(18)-C(19)-C(110)	120.0(5)
C(19)-C(110)-C(111)	121.2(5)
C(110)-C(111)-C(112)	120.0(5)
C(17)-C(112)-C(111)	118.1(5)
C(18)-C(17)-C(112)	121.3(4)
P(1)-C(113)-C(114)	118.5(3)
P(1)-C(113)-C(118)	121.1(3)
C(113)-C(114)-C(115)	118.8(4)

Continued

Table 29. Continued.

Bonds	Bond Angle, ($^{\circ}$), with Standard Deviation in Parentheses
C(114)-C(115)-C(116)	121.4(4)
C(115)-C(116)-C(117)	120.7(5)
C(116)-C(117)-C(118)	118.8(5)
C(113)-C(118)-C(117)	119.7(4)
C(114)-C(113)-C(118)	120.5(4)
P(2)-N(2)-C(219)	118.2(3)
P(2)-N(2)-C(220)	126.3(3)
C(219)-N(2)-C(220)	113.3(4)
C(21)-P(2)-N(2)	109.8(2)
C(27)-P(2)-N(2)	109.8(2)
C(213)-P(2)-N(2)	110.4(2)
C(21)-P(2)-C(27)	111.0(2)
C(21)-P(2)-C(213)	110.7(2)
C(27)-P(2)-C(213)	105.1(2)
P(2)-C(21)-C(22)	122.3(4)
P(2)-C(21)-C(26)	117.7(4)
C(21)-C(22)-C(23)	119.4(5)
C(22)-C(23)-C(24)	120.8(5)
C(23)-C(24)-C(25)	119.9(5)
C(24)-C(25)-C(26)	119.8(5)
C(21)-C(26)-C(25)	120.0(5)
C(22)-C(21)-C(26)	119.9(5)
P(2)-C(27)-C(28)	121.4(4)
P(2)-C(27)-C(212)	117.0(4)
C(27)-C(28)-C(29)	117.4(5)
C(28)-C(29)-C(210)	122.2(5)
C(29)-C(210)-C(211)	118.7(5)
C(210)-C(211)-C(212)	120.9(5)
C(27)-C(212)-C(211)	119.3(5)

Continued

Table 29. Continued.

Bonds	Bond Angle, ($^{\circ}$), with Standard Deviation in Parentheses
C(28)-C(27)-C(212)	121.4(5)
P(2)-C(213)-C(214)	120.0(4)
P(2)-C(213)-C(218)	118.4(4)
C(213)-C(214)-C(215)	117.7(5)
C(214)-C(215)-C(216)	121.9(5)
C(215)-C(216)-C(217)	120.7(6)
C(216)-C(217)-C(218)	118.7(6)
C(213)-C(218)-C(217)	119.5(6)
C(214)-C(213)-C(218)	121.3(5)
F(11)-B(1)-F(12)	102.9(6)
F(11)-B(1)-F(12a)	108.8(5)
F(11)-B(1)-F(13)	115.4(13)
F(11)-B(1)-F(13a)	102.2(12)
F(11)-B(1)-F(14)	99.8(5)
F(11)-B(1)-F(14a)	115.0(6)
F(12)-B(1)-F(13)	116.6(14)
F(12)-B(1)-F(14)	108.7(6)
F(12a)-B(1)-F(14a)	110.7(7)
F(13)-B(1)-F(14)	111.8(14)
F(13a)-B(1)-F(14a)	110.2(12)
F(21)-B(2)-F(22)	100.6(9)
F(21)-B(2)-F(23)	113.6(9)
F(21)-B(2)-F(24)	124.5(13)
F(21a)-B(2)-F(22a)	101.0(15)
F(21a)-B(2)-F(23a)	119.3(10)
F(21a)-B(2)-F(24a)	109.9(10)
F(21b)-B(2)-F(22b)	101.7(9)
F(21b)-B(2)-F(23b)	93.4(7)
F(21b)-B(2)-F(24b)	153.7(19)

Continued

Table 29. Continued.

Bonds	Bond Angle, (°), with Standard Deviation in Parentheses
F (22) -B (2) -F (23)	106.7 (11)
F (22) -B (2) -F (24)	87.9 (18)
F (22a) -B (2) -F (23a)	117.6 (20)
F (22a) -B (2) -F (24a)	81.8 (21)
F (22b) -B (2) -F (23b)	123.7 (9)
F (22b) -B (2) -F (24b)	69.1 (28)
F (23) -B (2) -F (24)	115.9 (13)
F (23a) -B (2) -F (24a)	120.0 (11)
F (23b) -B (2) -F (24b)	112.3 (21)

the boron, nitrogen, methyl carbon and phosphorus atoms. Planar angles in the borane adduct are presented in Table 30. Planes in the phosphonium cations are defined as follows: plane 1 contains carbon atoms C(11)-C(16); plane 2 contains carbon atoms C(17)-C(112); plane 3 contains carbon atoms C(113)-C(118); plane 4 contains atoms P(1), N(1), C(119) and C(120); plane 5 contains carbon atoms C(21)-C(26); plane 6 contains carbon atoms C(27)-C(212); plane 7 contains carbon atoms C(213)-C(218); plane 8 contains atoms P(2), N(2), C(219) and C(220). Planar angles in the phosphonium cations are presented in Table 31.

In general, bond angles containing phosphorus as the center are all in the range of what is expected for a tetrahedral geometry. Bond pair-bond pair repulsions would be most pronounced between the P-N multiple bond and the P-C single bonds. These repulsions can be used to explain the small increase in the N-P-C and decrease in the C-P-C bond angles from the value expected for a perfect tetrahedron. The N-B bond length corresponds well with N-B bond lengths reported for BH_3 and BF_3 adducts of amines (56). It was not possible to locate the exact positions of the fluorine atoms because of thermal motion in the solid. Therefore, the data and structures of the tetrafluoroborate anions are not absolute. This is reflected in the large standard deviations of the reported numbers. The major difference in the two cation structures is the orientation of the phenyl groups in space.

Table 30. Planar Angles in N-Methyliminotriphenylphosphorane Borane.

Planes	Planar Angle, (°)
1-2	86.7
2-3	70.5
1-3	111.9
4-1	69.3
4-2	113.0
4-3	63.8

Table 31. Planar Angles in N,N-Dimethylaminotriphenylphosphonium Ions.

Planes	Planar Angle, (°)
1-2	60.3
2-3	60.1
1-3	115.9
4-1	94.1
4-2	110.1
4-3	85.7
5-6	64.3
6-7	101.1
5-7	57.8
8-5	101.8
8-6	74.2
8-7	70.6

By comparing the observed P-N bond lengths to P-N bond lengths in compounds having varying amounts of π multiple bonding, some estimate on the degree of π overlap can be made. The sum of the single covalent radii is 1.76 \AA , and in the phosphoramidate ion the P-N bond length is 1.78 \AA (45). These lengths represent the lower limit of no multiple bonding between phosphorus and nitrogen. Wilson and Carroll (76) reported the crystal structure of the six membered ring compound $(\text{Cl}_2\text{PN})_3$. They found that all the P-N bond lengths were equal to 1.59 \AA and that the ring was essentially planar. Dougill (77) reported the crystal structure of an eight membered ring compound $[(\text{CH}_3)_2\text{PN}]_4$. The P-N bond distances were found to all be equal to 1.60 \AA , but the ring was puckered. Since these structure should contain alternating single and double bonds in the absence of any aromaticity, the P-N bond lengths represent a P-N bond order of approximately 1.5. This bond order neglects overlap from the sp^2 lone pairs. A crystal structure of N-parabromophenyl-iminotriphenylphosphorane gives a P-N bond distance of 1.567 \AA (78). This distance is less than the P-N distances in the cyclic compounds and thus probably represents a bond order of approximately 2.

The P-N bond lengths obtained in the current research program are greater than the P-N double bond lengths discussed so far. This would imply a bond order less than 1.5. Since the P-N bond lengths are significantly less than the sum of covalent radii, a bond order greater than unity

is implied. It was observed that the P-N bond length in the cation is larger than the P-N bond length in the borane adduct. Since phosphorus is less electronegative than nitrogen, the phosphorus atom can polarize electron density to shift more of the positive charge its way and thus reduce the π overlap and lengthen the P-N bond.

Pi-Bond Character Measured from P^{31} NMR Chemical Shifts

The amount of π bonding between phosphorus and atoms directly bonded to phosphorus can be estimated by using P^{31} nmr chemical shifts. Letcher and Van Wazer (48) derived a simple equation for quadruply connected phosphorus relating the P^{31} chemical shift, δ , referenced to 85% phosphoric acid, to two variables, α_1 and n_π , representing contributions to the shift by sigma and pi bonding respectively.

$$\delta = 11,828.5 - 7940\alpha_1 - 149n_\pi \quad (7.1)$$

The term n_π represents the total occupation of the $d\pi$ orbitals of phosphorus, in electronic charge per phosphorus atom. By rearranging equation (7.1), n_π can be solved for.

$$n_\pi = \frac{-\delta + 11,828.5 - 7940\alpha_1}{149} \quad (7.2)$$

In equation (7.2), the variable α_1 , must be calculated for every individual molecule in order to solve for n_π . A

short computer program developed by Letcher and Van Wazer (48) was used to calculate these values. The program was modified for use on an Apple II computer, and an additional line was included employing the calculated value of α_1 to calculate n_π via equation (7.2). A copy of the modified program is presented in the Appendix for N-ethylimino-triphenylphosphorane.

The parameter, α_1 , represents the shielding of the P^{31} nucleus by electrons in σ bonding orbitals around phosphorus. In all but a few of the known phosphorus compounds it appears that σ bonds involve only the s and p orbitals. The contribution of the σ bonds to the P^{31} nmr shift in such molecules is a function of the bond polarities and the molecular geometry around phosphorus. The calculation of α_1 takes into account the geometry around phosphorus and the electronegativities of the substituents directly attached to the phosphorus. The bond angle values were obtained from the crystal structure of N-methylimino-triphenylphosphorane borane, and the values were not changed when going from one M group to another. It was assumed that minor changes in the structure of M will not change the MPZ and MPT bond angles significantly. The values that must be changed in each calculation, for different M groups, are the electronegativity of the M group and the P^{31} nmr chemical shift.

Group electronegativities were calculated by the method of Huheey (79) using orbital electronegativities defined (80) as

$$\chi = a + b\delta$$

where a is the inherent electronegativity; b is the charge coefficient, and δ is the partial charge resulting from electron gain or loss. The parameters a and b are defined as

$$a = \frac{I - A}{2}$$

$$b = I + A$$

where I is the ionization energy and A is the electron affinity. This method provides electronegativities on the Mulliken scale which must be converted (81) to the Pauling scale by $\chi_p = 0.336(\chi_m - 0.615)$ for use in deriving α_1 values. The value for the group orbital electronegativity of C_6H_5 was calculated as 2.49 on the Pauling scale, using the value $a = 8.03$ (82). The other group orbital electronegativities were calculated employing a and b values calculated (83) for a sp^2 hybrid nitrogen atom and a and b values from compiled data of Huheey (79,82). It was assumed that BH_3 was coordinated to the α nitrogen atom in group electronegativity calculations for borane adducts of the

β -N-substituted-aminoiminotriphenylphosphoranes. Values for the calculated group electronegativities, for α_1 , and for n_π are presented in Table 32. The changes in π bonding upon coordination of the phosphoranes by BH_3 are given by Δn_π in Table 33.

Discussion of P^{31} NMR Derived Data

It was observed that by changing the group electronegativity, the value of α_1 does not change significantly. Thus, the general downfield shift of the P^{31} nmr resonances on complexation by BH_3 must be entirely due to a change in π bonding. It was also observed that χ_p decreases and n_π increases as the alkyl groups get larger, for the N-alkyliminotriphenylphosphoranes. A decrease in the group electronegativity should cause the 2p electron cloud on nitrogen to be more diffuse and thus decrease the π overlap with this orbital. An increase in the alkyl group size should cause an increase in the back strain from steric crowding with the phenyl groups. This should increase the P-N-C bond angles and thus cause more π overlap with the lone pair orbital on nitrogen. Therefore, the observed trends in the phosphorane data imply that some π overlap with the sp^2 hybridized lone pair occurs. The differences in the amount of π overlap, in the N-alkyliminotriphenylphosphoranes, parallels their relative base strengths as measured in Chapter VI. An increase in π overlap corresponds to a decrease in relative basicity.

Table 32. Parameters Used in and Results of Equation (7.2)
for $(C_6H_5)_3PM$.

M Group	χ_p	α_1	n_π
$N(CH_3)$	2.59	1.49572	-0.266
$N(C_2H_5)$	2.48	1.49624	-0.323
$N(n-C_3H_7)$	2.43	1.49648	-0.335
$N(i-C_3H_7)$	2.43	1.49648	-0.363
$N(i-C_4H_9)$	2.40	1.49661	-0.343
$N(t-C_4H_9)$	2.40	1.49661	-0.461
$N(CH_3)_2$	2.54	1.49592	-0.00920
$NN(CH_3)_2$	2.55	1.49592	-0.225
$NNH(C_6H_5)$	2.66	1.49544	-0.177
$NN(CH_3)(C_6H_5)$	2.58	1.49575	-0.222
$N(CH_3)BH_3$	2.34	1.49689	-0.139
$N(C_2H_5)BH_3$	2.33	1.49695	-0.151
$N(n-C_3H_7)BH_3$	2.32	1.49699	-0.152
$N(i-C_3H_7)BH_3$	2.32	1.49699	-0.169
$N(i-C_4H_9)BH_3$	2.32	1.49701	-0.151
$N(t-C_4H_9)BH_3$	2.32	1.49701	-0.233
$NN(CH_3)_2BH_3$	2.40	1.49662	-0.122
$NNH(C_6H_5)BH_3$	2.51	1.49608	-0.0681
$NN(CH_3)(C_6H_5)BH_3$	2.47	1.49625	-0.0711

Table 33. Change in π -Bonding on Coordination of Phosphoranes by BH_3 .

Phosphorane	Δn_{π}
$(\text{C}_6\text{H}_5)_3\text{PNCH}_3$	-0.127
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{C}_2\text{H}_5)$	-0.171
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{n-C}_3\text{H}_7)$	-0.183
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{i-C}_3\text{H}_7)$	-0.194
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{i-C}_4\text{H}_7)$	-0.192
$(\text{C}_6\text{H}_5)_3\text{PN}(\text{t-C}_4\text{H}_7)$	-0.228
$(\text{C}_6\text{H}_5)_3\text{PNN}(\text{CH}_3)_2$	-0.103
$(\text{C}_6\text{H}_5)_3\text{PNNH}(\text{C}_6\text{H}_5)$	-0.109
$(\text{C}_6\text{H}_5)_3\text{PNN}(\text{CH}_3)(\text{C}_6\text{H}_5)$	-0.151

The change in π bonding, Δn_{π} , upon complexation by BH_3 , shows a decrease in π overlap upon adduct formation. This is probably due to a combination of a decrease in group electronegativity and removal of the sp^2 lone pair from possible π overlap. It was also observed that an increase in the alkyl group size causes an increase in the magnitude of Δn_{π} .

Errors and Reliability in P^{31} NMR Derived Data.

It was assumed in calculations of α_1 values that the bond angles around phosphorus do not change significantly with minor changes in the M group. Comparisons of N-P-C bond angles in the structures of the N,N-dimethylamino-triphenylphosphonium ions and in the structure of N-para-bromophenyl-iminotriphenylphosphorane (78), with the N-P-C bond angles in the borane adduct, show that the angles in the cations and phosphorane are within $\pm 5^\circ$ of the corresponding borane adduct angles. Since P^{31} nmr shifts are recorded on dissolved samples, the angles around phosphorus should average out. To determine the significance of differences in the angles, EA and EP were varied in calculations of α_1 for $\text{M} = \text{N}(\text{CH}_3)\text{BH}_3$. The values of EA and EP used and the corresponding calculated values of α_1 are presented in Table 34.

Since $\alpha = f(\chi_p, \text{EA}, \text{EP})$ then

$$\Delta\alpha = \frac{d\alpha}{d\chi_p} \Delta\chi_p + \frac{d\alpha}{d\text{EA}} \Delta\text{EA} + \frac{d\alpha}{d\text{EP}} \Delta\text{EP}.$$

Table 34. Effect of Changing Angles EA and EP on the Value of α_1 for $M = N(CH_3)BH_3$.

EA	Angles ($^\circ$)	EP	α_1
107		114.6	1.49697
108		114.6	1.49695
109		114.6	1.49693
110		114.6	1.49690
111		114.6	1.49688
112		114.6	1.49686
113		114.6	1.49683
114		114.6	1.49681
110.7		107	1.49697
110.7		108	1.49696
110.7		109	1.49695
110.7		110	1.49694
110.7		111	1.49693
110.7		112	1.49692
110.7		113	1.49691
110.7		114	1.49690

The sum of the partial derivatives, $\frac{d\alpha}{d\chi_p} + \frac{d\alpha}{dEA} + \frac{d\alpha}{dEP}$ gives the maximum error in the calculated α_1 values. By holding combinations of $\Delta\chi_p$, ΔEA and ΔEP constant, the partial derivatives can be solved. By using data from Tables 32 and 34, the partial derivatives were solved. They are as follows: $\frac{d\alpha}{d\chi_p} = 3.79 \times 10^{-3}$, $\frac{d\alpha}{dEA} = 2.09 \times 10^{-5}$, $\frac{d\alpha}{dEP} = 1.01 \times 10^{-5}$. The sum is 3.82×10^{-3} . Therefore, the maximum error in the α_1 values is $\pm 3.82 \times 10^{-3}$. The major contribution to the

error in α_1 is from the calculated group electronegativities. The errors from small changes in the bond angles do not contribute very much to the total error in α_1 . Therefore, the assumption about changes in the bond angles is valid. Chemical shifts in P^{31} nmr are solvent dependent. Chemical shifts of the same compound in different solvents occur in a 4 ppm range. Therefore, the P^{31} nmr data presented in this study are relative to the solvent used, benzene. All calculated values were not rounded off until the final calculation to reduce error propagation.

Conclusion

The P-N bond lengths and P^{31} nmr data both show a reduction in π bonding between phosphorus and nitrogen when N-substituted-iminotriphenylphosphoranes are complexed to BH_3 . In addition, the P-N bond length data show even less π overlap in the cation than in the borane adduct. Comparison of the two methods to measure π overlap reveals that both have advantages and disadvantages over the other. The crystallographic data probably represent a more accurate determination of multiple bonding but are time consuming and require the availability of suitable crystalline samples. The P^{31} nmr measurements have the advantage of being quick and easily accessible. The P^{31} nmr derived data provide numbers which can be useful in describing physical properties such as basicity. However, the accuracy of the numbers must be kept in mind when using them.

CHAPTER VIII

REDUCTION OF IMINOTRIPHENYLPHOSPHORANE AND N,N-DIMETHYL-AMINOTRIPHENYLPHOSPHONIUM ION

Amino and iminotriphenylphosphoranes contain phosphorus in the +5 oxidation state. Reactions involving reduction of this class of compounds have not been reported in the literature. Since ± 3 and $+4$ are stable oxidation states of phosphorus, reduction of iminotriphenylphosphoranes and their derivatives should be possible using appropriate reducing agents. It is expected that the ease of reduction of these compounds should be dependent on the amount of $d\pi-p\pi$ overlap between phosphorus and nitrogen. An increase in overlap should cause more electron density to be around the phosphorus atom, and thus a decrease in its reactivity toward reduction is expected. To test this hypothesis, three experiments were performed using iminotriphenylphosphorane and N,N-dimethylaminotriphenylphosphonium iodide with tetra-n-butyl-ammonium borohydride, lithium borohydride or sodium dimethylaminoborohydride as reducing agents.

Reaction of Iminotriphenylphosphorane With
Tetra-n-Butyl-Ammonium Borohydride

Iminotriphenylphosphorane, 1.4601 g (5.2655 mmoles), and tetra-n-butyl-ammonium borohydride, 1.3593 g (5.2827 mmoles), were combined with 25 ml of dry benzene in a 50 ml round bottom flask. The flask was equipped with a reflux condenser connected to a T-tube. The T-tube was attached to a dry nitrogen source on one side and a U-tube trap on the other side. The end of the trap was connected to a mercury bubbler. The solution was stirred and heated to reflux for 22 days. Dry nitrogen was passed over the reaction mixture and through the trap which was kept at -196° . Samples were removed from the reaction flask periodically, and P^{31} nmr spectra were measured to determine the progress of the reaction. The reaction was terminated when the peak corresponding to iminotriphenylphosphorane had completely disappeared.

The flask was allowed to cool to room temperature, precipitating a white solid. The flask was stoppered and transferred to a dry box. The solid was filtered and the filtrate was saved.

Identification of Species in the Filtrate

Approximately one half of a milliliter of the filtrate was transferred to a nmr tube. A H^1 nmr spectrum was recorded and showed peaks corresponding to tetra-n-butyl-ammonium ion, borohydride ion, tri-n-butylamine and peaks in the phenyl region. A P^{31} nmr spectrum was recorded and

showed a major peak at 4.718 ppm corresponding to triphenylphosphine and a broad minor resonance at -22.244 ppm corresponding to triphenylphosphine borane. The ratio of the integrated areas under the peaks was 2.69 to 1. A B^{11} nmr spectrum was recorded proton coupled and showed only peaks corresponding to borohydride ion. The peaks corresponding to triphenylphosphine borane were not observed in the B^{11} nmr spectrum. The concentration of triphenylphosphine borane was too low to produce an observable signal in the overlapping borohydride quintet.

The filtrate was then combined with trimethylamine borane, 0.1596 g (2.188 mmoles). Approximately one half of a milliliter of the resulting solution was transferred to a nmr tube. A B^{11} nmr spectrum was recorded proton decoupled and showed two peaks corresponding to trimethylamine borane and borohydride ion. The ratio of the integrated areas under the peaks revealed that approximately 2.36 mmoles of borohydride remained in the filtrate (44.7%).

Identification of Gaseous Products

After the flask was removed from the condenser, the trap was sealed from the atmosphere and then evacuated, maintaining a temperature of -196° . The trap was sealed, and the frozen contents were allowed to warm to room temperature. Two liquid phases remained in the trap. A gas sample was removed from the trap, and a GC was recorded using a 2.5 meter long column 1/4 inch in diameter packed

with Porapak-Q. The heating program employed was 40° initially for 5 minutes followed by a ramp of +10° per minute until the temperature reached 200°. The temperature was kept at 200° for 15 minutes. The GC trace showed six peaks of which three were identified by their retention times as nitrogen, carbon dioxide and benzene. A second gas sample was removed from the trap, and a GC-mass spectrum was recorded using a 5 foot long column 2 millimeters in diameter packed with Porapak-Q. The heating program employed was 50° initially then a ramp of +10° per minute until the temperature reached 250°. The three unidentified peaks were found to be water, n-butane and butene, by their mass spectra. The mass spectra of the isomers of butene are almost identical so that a distinction between them could not be made (68).

Identification of Solid

The weight of the precipitate was 0.6675 g. The solid was recrystallized from dry benzene to produce white cubic crystals. The recovered material weighed 0.5660 g (85% yield), mp 203-204°. The compound was characterized by a combination of IR, H^1 , P^{31} , B^{11} and C^{13} nmr, elemental analyses and mass spectral data.

The IR spectrum of the solid is reproduced in Figure 40. The infrared assignments of iminotriphenylphosphorane and the solid are given in Table 35. The various

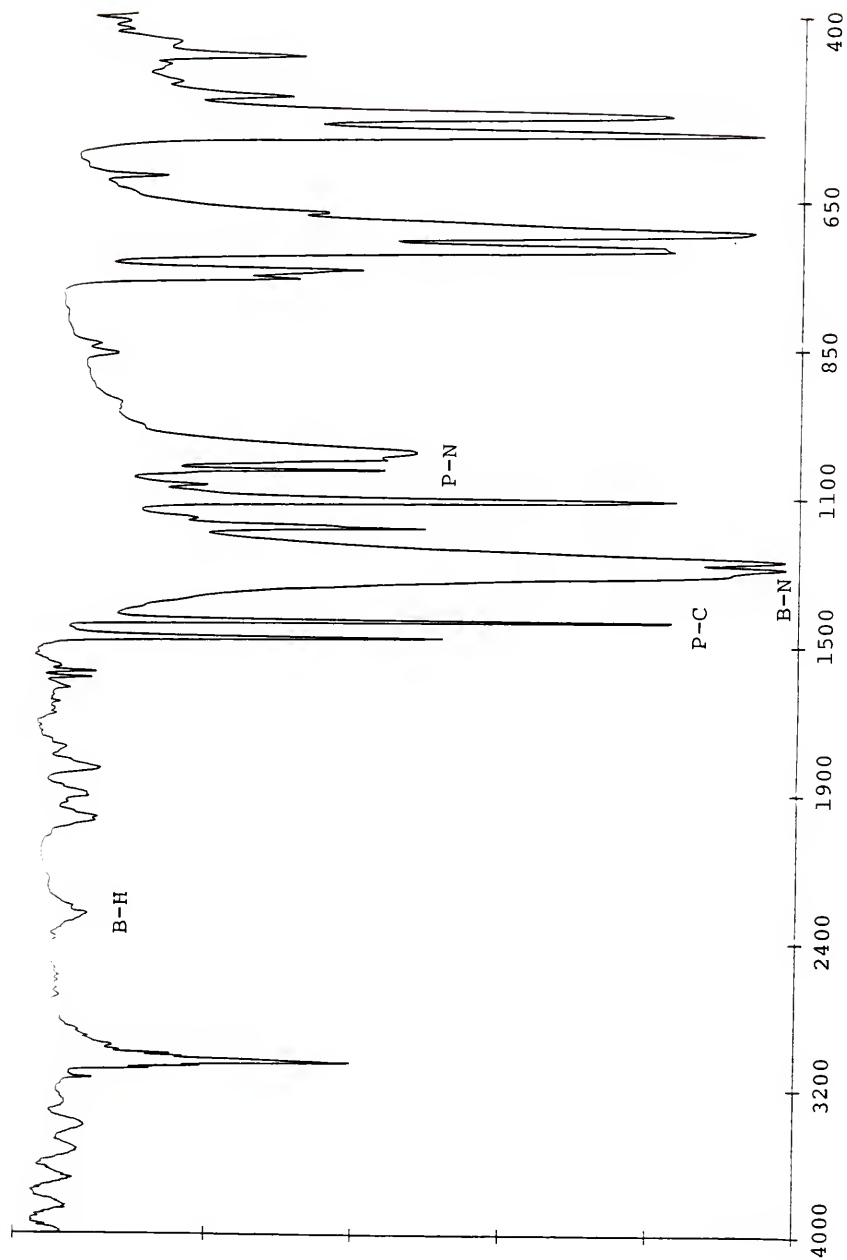


Figure 40. Infrared spectrum of $[(C_6H_5)_3PN]_2BH$.

Table 35. Infrared Data of Iminotriphenylphosphorane and Product from Reaction with Tetra-n-Butyl-Ammonium Borohydride.

Compounds	P-C Stretch cm ⁻¹	P-N Stretch cm ⁻¹	B-H Stretch cm ⁻¹	B-N Stretch cm ⁻¹	N-H Stretch cm ⁻¹
(C ₆ H ₅) ₃ PNH	1436	877 ^a	--	--	3353
Product	1434	998	2251 ^b	1286	--

^abroad; ^bvery weak.

infrared assignments were made by a straightforward comparison of the two spectra. The infrared spectrum of the solid provided valuable information on its structure. The absence of a N-H absorption indicates that this structural element is missing. The presence of P-C, P-N and B-H absorptions indicates that these structural elements must be present. The large intensity and high frequency of the B-N absorption indicate appreciable double bond character between boron and nitrogen (84).

The H^1 nmr spectrum of the solid in deuterated methylene chloride showed only peaks in the phenyl region between 7.163 and 7.779 ppm. The P^{31} nmr spectrum of the same sample showed only one peak at -0.487 ppm. The B^{11} nmr spectrum, proton coupled, showed only a very broad resonance at -17.724 ppm with no multiplicity. The peak did not change significantly when the spectrum was run proton decoupled. The half-width of the peak was approximately 899 Hz. The chemical shift of the resonance indicates a sp^2 bonded boron atom (73).

An expansion of the C^{13} nmr spectrum of the solid is reproduced in Figure 41. The C^{13} chemical shifts and phosphorus to carbon coupling constants are presented in Table 36. The peak occurring at 128.758 ppm corresponds to the chemical shift of benzene in deuterated methylene chloride. Therefore, the solid must crystallize with benzene of solvation in the crystal lattice. The rest of

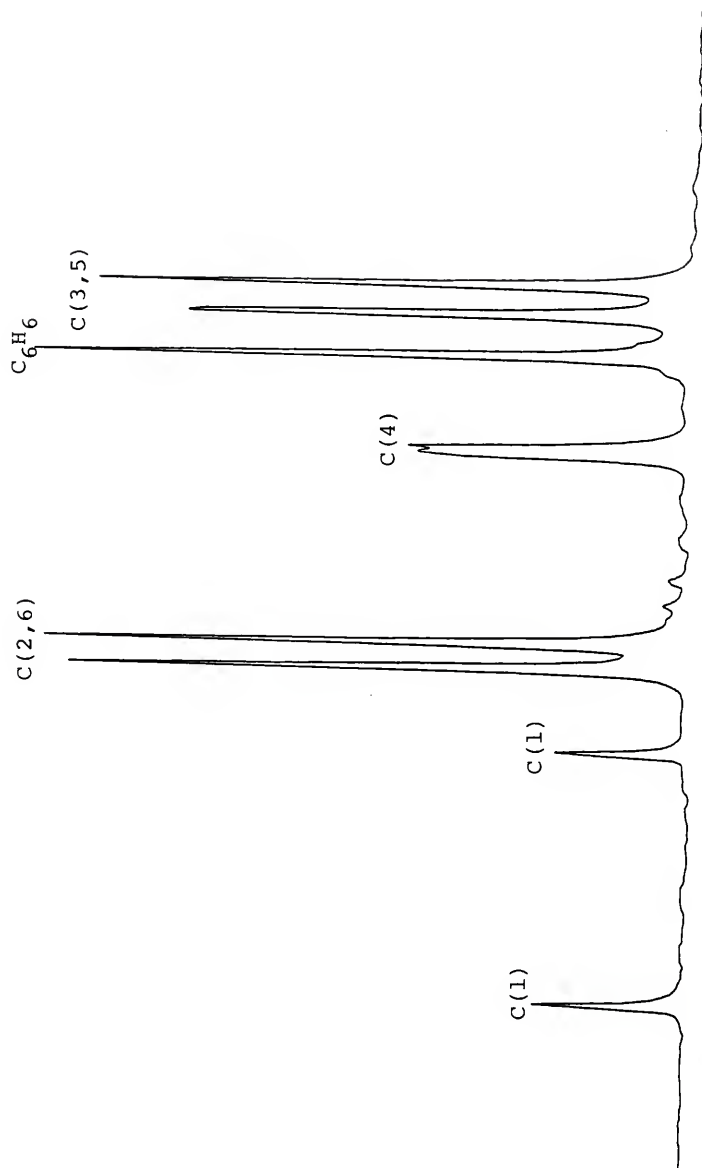


Figure 41. ^{13}C nmr spectrum of $[(\text{C}_6\text{H}_5)_3\text{PN}]_2\text{BH}$.

Table 36. ^{13}C NMR Data of Solid Obtained by Reaction of Iminotriphenylphosphorane with Tetra-n-Butyl-Ammonium Borohydride.

Structural Unit		^{13}C Resonances δ , ppm and Coupling Constants J, Hz	
		δ C-1	δ C-2/6
C ³ C ²			δ C-3/5
			δ C-4
C ⁴		136.678	133.291
	C ¹ - P		
		J _{P-C} = 96.44 Hz	J _{P-C} = 9.76 Hz
	C ₅ C ₆		
		J _{P-C} = 12.21 Hz	J _{P-C} = 2.45 Hz

the C^{13} spectrum is consistent with phosphorus-attached phenyl rings (72,85).

Elemental analyses were performed on a solvated sample and on a sample which had been heated to 80° in vacuo for 12 hours. The analysis of the solvated sample was: %C 80.24, %H 6.04; %N 3.73, and the analysis for the unsolvated sample was: %C 75.96, %H 5.41, %N 4.68.

The mass spectrum of the solid is reproduced in Figure 42. The mass intensity data are presented in Table 37. The highest mass peak at 563 is most likely a M-1 peak derived from the unobserved molecular ion by rupture of a B-H bond. This would indicate that the molecular weight of the material, minus the benzene, must be 564. Other peaks of interest in the spectrum are 276, corresponding to $(C_6H_5)_3PN^+$, and 262, corresponding to $(C_6H_5)_3P^+$.

It was deduced from the combination of accumulated data on the solid that its formula must be $[(C_6H_5)_3PN]_2BH$. The calculated CHN analysis of: %C 76.61, %H 5.54, %N 4.96 agrees well with that obtained for the unsolvated sample. Furthermore, if two moles of benzene are assumed per mole of deduced formula, the calculated CHN analysis of: %C 80.00, %H 6.01, %N 3.89 agrees well with that obtained for the solvated sample. The % yield of the crude product is 35% based on iminotriphenylphosphorane.

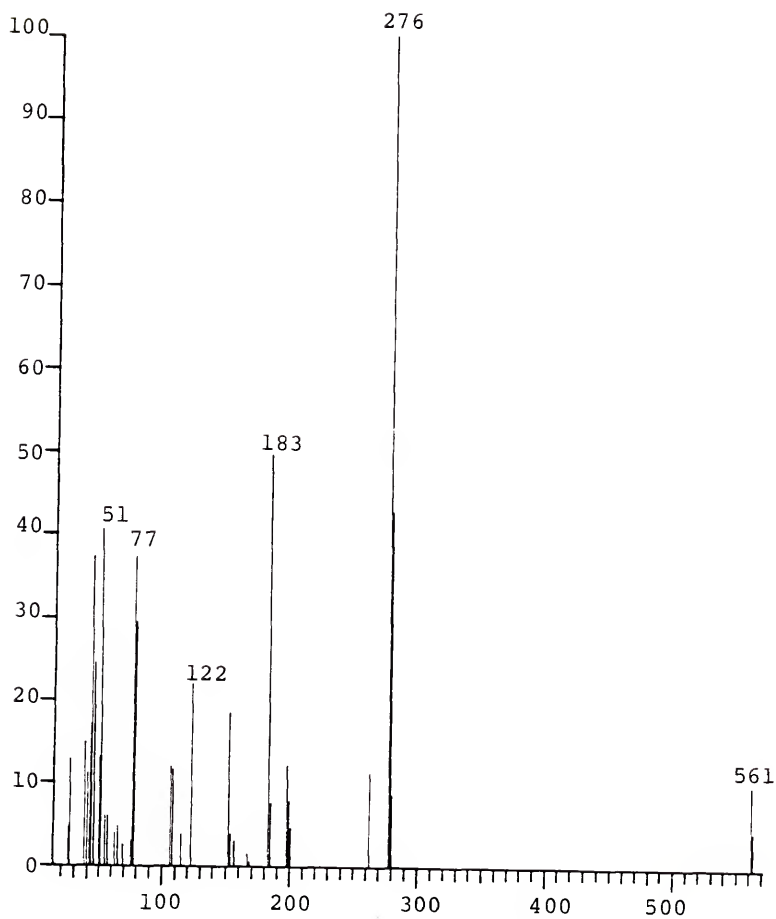


Figure 42. Mass spectrum of $[(C_6H_5)_3PN]_2BH$.

Table 37. Mass Intensity Data of Solid Obtained by Reaction of Iminotriphenylphosphorane with Tetra-n-Butyl-Ammonium Borohydride.

Mass	Absolute Intensity	% Intensity of 276
563	303	4.86
562	260	4.17
561	650	10.43
278	542	8.70
277	2660	42.68
276	6232	100.00
262	701	11.25
201	284	4.56
200	454	7.28
199	495	7.94
198	756	12.13
185	481	7.72
184	405	6.50
183	3091	49.60
168	28	0.45
167	97	1.56
157	188	3.02
154	246	3.95
153	330	5.30
152	1167	18.73
122	1370	21.98
115	247	3.96
108	736	11.81
107	758	12.16
78	1845	29.61
77	2329	37.37
76	197	3.16
69	159	2.55

Continued

Table 37. Continued.

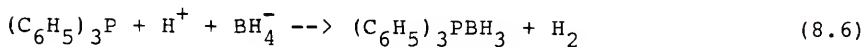
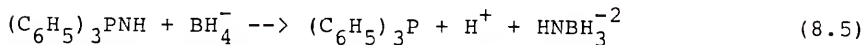
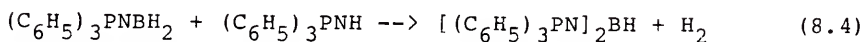
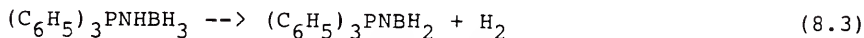
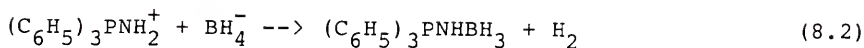
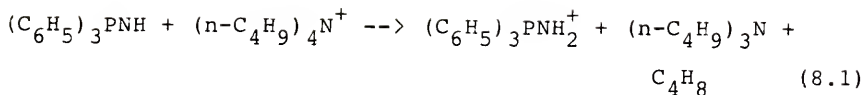
Mass	Absolute Intensity	% Intensity of 276
65	307	4.93
63	261	4.19
57	385	6.18
55	386	6.19
52	434	6.96
51	2532	40.63
50	835	13.40
46	1538	24.68
44	2322	37.26 [*]
43	1061	17.03 [*]
41	699	11.22
39	942	15.12

^{*} Metastable ions

Discussion of Reaction Products

It was found that both iminotriphenylphosphorane and tetra-n-butyl-ammonium borohydride are both stable in refluxing benzene for periods exceeding 1 week. Therefore, the observed products must be due to the reaction of imino-triphenylphosphorane with tetra-n-butyl-ammonium borohydride. The observation of tri-n-butylamine, butene and butane as reaction products means that proton abstraction on the β -carbon atom of the tetra-n-butyl-ammonium ion must have taken place. This reaction is analogous to the Hoffmann elimination reaction observed in tetra-alkyl-ammonium hydroxides. In the current investigation, the base would be either iminotriphenylphosphorane or some product resulting from reduction of iminotriphenylphosphorane. Butane could be produced by reduction of butene by borohydride ion. The amount of boron left in solution and contained in the solid product comes to a total of only 3.286 mmoles. Thus, approximately 1.996 mmoles (38%) of the boron started with is unaccounted for.

The presence of triphenylphosphine as one of the reaction products indicates that reduction of phosphorus must have taken place. The reduction reaction would provide a source of protons which could produce diborane. The diborane could then react with triphenylphosphine to produce the observed product, triphenylphosphine borane. A possible reaction sequence to explain the observed products is as follows.



The final reaction product, borazine (86), would distill over to the trap and be decomposed by the water there. This would explain the unaccounted for boron loss.

Reaction of N,N-Dimethylaminotriphenylphosphonium
Iodide With Sodium Dimethylaminoborohydride

Sodium dimethylaminoborohydride as the dioxane solvate, 0.6964 g (5.574 mmoles), and N,N-dimethylaminotriphenylphosphonium iodide, 2.4115 g (5.5658 mmoles), were combined with 25 ml of dry monoglyme in a 50 ml round bottom flask. The flask was equipped with a reflux condenser connected to a T-tube. The T-tube was attached to a dry nitrogen source on one end and a mercury bubbler on the other end. The two-phase mixture was stirred and heated to reflux for 24 hours under a dry nitrogen atmosphere. The flask was allowed to cool to room temperature. A white solid was present in the cooled mixture. The flask was stoppered and transferred to a dry box. The solid was filtered and dried in vacuo. The filtrate was saved.

Identification of the Species in the Filtrate

Approximately one half of a milliliter of the filtrate was transferred to a nmr tube. A P^{31} nmr spectrum was recorded and showed only one peak corresponding to triphenylphosphine in the same solvent. Boron-11 nmr spectra were recorded proton decoupled and proton coupled and showed two sets of resonances. The peaks were identified by their chemical shifts and coupling constants as bis(dimethylamino) borane (87) and dimethylamine borane (73). The ratio of the integrated areas under the peaks was 1:1. Since no peak was found in the B^{11} nmr spectrum corresponding to sodium

dimethylaminoborohydride in monoglyme, the reaction had reached completion.

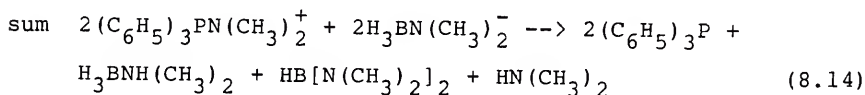
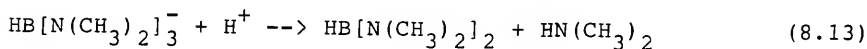
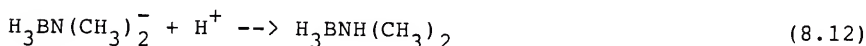
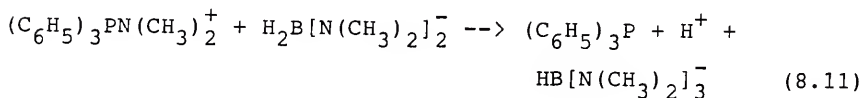
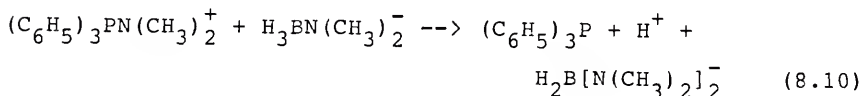
Identification of Solid

The weight of the solid after drying was 0.1811 g. A portion of the solid was dissolved in deuterated methylene chloride. The solution was placed into a nmr tube, and P^{31} and H^1 nmr spectra were recorded. The P^{31} and H^1 nmr spectra showed only peaks corresponding to N,N-dimethylaminotriphenylphosphonium iodide in the same solvent. Therefore, the recovered solid corresponded to 8% of unreacted starting material.

Discussion of Reaction Products

It was found that dimethylamine borane is stable in refluxing monoglyme for a period of 3 days. Therefore, bis(dimethylamino) borane could not have been produced by decomposition of dimethylamine borane (54,55,88). The absence of triphenylphosphine borane as a reaction product indicates that diborane was not produced in the reaction. Since triphenylphosphine was identified as the only phosphorus containing product of the reaction, N,N-dimethylaminotriphenylphosphonium iodide was almost quantitatively reduced to triphenylphosphine. The observation of dimethylamine borane as a reaction product provides evidence for the production of protons in the reduction reaction. Sodium dimethylaminoborohydride was found to react with

N-isopropylaminotriphenylphosphonium bromide to produce exclusively, dimethylamine borane, N-isopropyliminotriphenylphosphorane and sodium bromide. Since half of the dimethylaminoborohydride was converted to dimethylamine borane, an intermediate reducing agent must have been produced during the reaction. This reducing agent must have reacted further to produce bis(dimethylamino) borane. A possible reaction sequence to explain the observed products is as follows.



The sum of the individual reactions corresponds to the observed distribution of boron containing products. The dimethylamine produced in equation (8.13) would distill away from the reaction flask and would not have been observed.

Reaction of N,N-Dimethylaminotriphenylphosphonium
Iodide With Lithium Borohydride

Lithium borohydride, 0.1218 g (5.592 mmoles), and N,N-dimethylaminotriphenylphosphonium iodide, 2.2705 g (5.2404 mmoles), were combined with 25 ml of dry monoglyme in a 50 ml round bottom flask. The flask was equipped with a reflux condenser connected to a T-tube. The T-tube was attached to a dry nitrogen source on one end and a mercury bubbler on the other end. The outlet of the mercury bubbler was connected to a bubbler containing an aqueous solution of silver nitrate. The two phase mixture was stirred and heated to reflux for 47 hours under a dry nitrogen atmosphere. The flask was allowed to cool to room temperature. A white solid was present in the cooled mixture. The flask was stoppered and transferred to a dry box. The solid was filtered and dried in vacuo. The filtrate was saved.

Identification of Species in the Filtrate

After 19 hours of refluxing, approximately one half of a milliliter of the mixture was filtered into a nmr tube. A P^{31} nmr spectrum was recorded and showed peaks corresponding to triphenylphosphine borane, triphenylphosphine and N,N-dimethylaminotriphenylphosphonium ion in the same solvent. The triphenylphosphine borane resonances were centered at -21.837 ppm. The boron to phosphorus coupling constant was 59 Hz. The N,N-dimethylaminotriphenylphosphonium ion peak occurred at -46.997 ppm. In addition, an unidentified multiplet centered at -71.011 ppm was observed.

Boron-11 nmr spectra were recorded proton decoupled and proton coupled and showed five resonances. The peaks were identified by their chemical shifts and coupling constants as dimethylamino borane dimer (73,89), bis(borane)dimethylamide anion (90), triphenylphosphine borane (29,91), dimethylamine borane (92) and borohydride ion. The presence of borohydride ion indicated that the reaction had not reached completion.

Approximately one half of a milliliter of the filtrate obtained after 47 hours was transferred to a nmr tube. A P^{31} nmr spectrum was recorded and showed peaks corresponding to triphenylphosphine borane and N,N-dimethylaminotriphenylphosphonium ion in the same solvent. The unidentified multiplet described before was also present as was a collection of unidentified peaks in the -54 to -60 ppm range. Boron-11 nmr spectra were recorded proton decoupled and proton coupled and showed three resonances. The peaks were identified by their chemical shifts and coupling constants as dimethylamino borane dimer, dimethylamine borane and triphenylphosphine borane. There also appeared to be some unidentified resonances overlapping with the triphenylphosphine borane peaks.

Identification of Solid

The weight of the solid after drying was 0.7305 g. A portion of the solid was dissolved in deuterated methylene chloride. The solution was placed into a nmr tube, and P^{31}

and ^1H nmr spectra were recorded. The ^{31}P and ^1H nmr spectra showed only peaks corresponding to N,N-dimethylaminotriphenylphosphonium iodide in the same solvent. Therefore, the recovered material corresponded to 32% of unreacted starting material.

Identification of Gaseous Products

It was observed that a black solid was produced in the silver nitrate bubbler during the reaction period. Thus, a volatile reducing agent was produced in the reaction flask. The reducing agent was most likely diborane or some other higher boron hydride.

Discussion of Reaction Products

The absence of borohydride ion in the final reaction mixture indicates that the reaction had reached completion. The absence of the bis(borane)dimethylamide anion in the final reaction product means that this species must have been an intermediate. The presence of triphenylphosphine as a product indicates that reduction of N,N-dimethylaminotriphenylphosphonium ion must have occurred. The observation of triphenylphosphine borane and bis(borane)dimethylamide ion in the reaction flask and reduction of silver ion give evidence for the production of diborane during the reaction. The presence of bis(borane)dimethylamide anion indicates that dimethylaminoborohydride was produced during the reaction.

Assuming all the reacted phosphorus was in solution, the integrated areas under the multiplet and the triphenylphosphine borane peaks in the final P^{31} nmr spectrum correspond to 0.830 and 2.14 mmoles respectively. The integrated areas under the N,N-dimethylaminotriphenylphosphonium ion peak and the resonances between -54 and -60 ppm correspond to 0.126 and 0.467 mmoles of phosphorus respectively.

To the filtrate was added 0.389 g (5.33 mmoles) of trimethylamine borane. Approximately one half of a milliliter of the resulting solution was transferred to a nmr tube. A B^{11} nmr spectrum was recorded proton decoupled. The ratios of the integrated areas under the peaks revealed that approximately 0.819 mmoles of dimethylamino borane dimer, 0.400 mmoles of dimethylamine borane and 2.58 mmoles of boron, under the peaks overlapping with the triphenylphosphine borane peaks, were present in the filtrate. The mass balance of the protons, amino groups and boron atoms in the reaction, for the observed products, is presented in Table 38.

Several reactions are possible with the materials present in the flask. Possible reactions in the system are as follows.

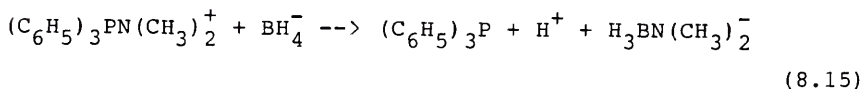
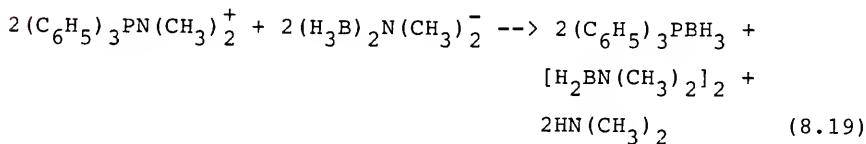
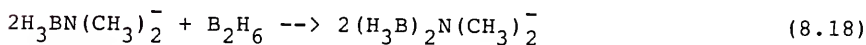
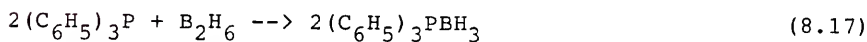
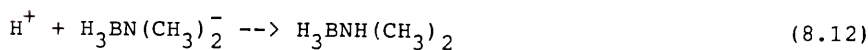
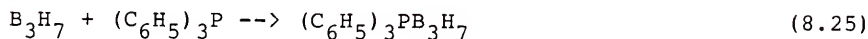
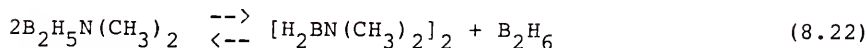
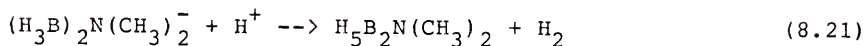
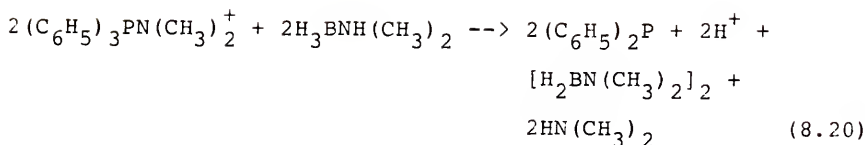


Table 38. Mass Balance.

Species	Proton mmoles	Amino mmoles	Boron mmoles
Starting Solution	3.563	3.563	5.592
$[\text{H}_2\text{BN}(\text{CH}_3)_2]_2$	0	1.64	1.64
$\text{H}_3\text{BNH}(\text{CH}_3)_2$	0.400	0.400	0.400
$(\text{C}_6\text{H}_5)_3\text{PBH}_3$	2.14	--	2.14
Peaks Overlapping with $(\text{C}_6\text{H}_5)_3\text{PBH}_3$ Resonances	--	--	0.44
Unaccounted for	1.02	1.52	0.97





The possible reaction products containing boron, along with their respective B^{11} nmr chemical shifts are presented in Table 39. Many of the proposed reactions cannot have occurred because the reactants or products were not observed in the B^{11} nmr spectra. These reactions are (8.21)-(8.25). Furthermore, reaction (8.20) would not be expected to have occurred since dimethylamino borane dimer was not a product in the reaction between N,N-dimethylaminotriphenylphosphonium ion and dimethylaminoborohydride. Dimethylaminoborohydride was not observed in the B^{11} nmr spectra. It must have been produced in the reaction sequence, however, because of the presence of bis(borane)dimethylamide (93) and dimethylamine borane. The dimethylaminoborohydride does

Table 39. Possible Reaction Products Containing Boron.

Compound	B^{11} NMR Chemical Shift*	Reference
$H_3BN(CH_3)_2^-$	32.9 ppm $J_{B-H} = 84$ Hz	92
$H_3BNH(CH_3)_2$	31.7 ppm $J_{B-H} = 95$ Hz	92
$(C_6H_5)_3PBH_3$	55.8 ppm $J_{B-H} = 98$ Hz $J_{B-P} = 57$ Hz	29
$(H_3B)_2N(CH_3)_2^-$	29.4 ppm $J_{B-H} = 91$ Hz	90
$[H_2BN(CH_3)_2]_2$	14.5 ppm $J_{B-H} = 116$ Hz	73
$H_5B_2N(CH_3)_2$	35.2 ppm $J_{B-H} = 130$ Hz (Terminal) $J_{B-H} = 30$ Hz (Bridge)	94
$B_3H_8^-$	46.5 ppm $J_{B-H} = 32$ Hz	73
$H_7B_3P(C_6H_5)_3$	35.8 ppm, 64.3 ppm $J_{B-P} = 97$ Hz	**

* Shifts are relative to trimethylborate with negative ppm downfield from trimethylborate.

** Measured at 64.184 MHz proton decoupled.

not participate as a reducing agent in this system because of the absence of bis(dimethylamino) borane as a product.

To account for the amino groups and protons which were undetected in the spectra, a reaction must have occurred to produce free dimethylamine. It is observed from Table 37

that the number of mmoles of unaccounted for amino groups roughly equals the number of mmoles of dimethylamino borane monomer units. Reaction (8.19) is consistent with the mass balance data, and this gives support for its occurrence. The unaccounted for boron from Table 38 was probably lost as volatile diborane.

The unidentified multiplet in the P^{31} nmr spectra at -71.011 ppm probably contains a triphenylphosphine group attached to a boron containing fragment. This would account for the multiplet nature of the P^{31} resonance and the B^{11} resonances which overlap with the triphenylphosphine borane peaks. If the assumption about the structure is correct, then the mass balance indicates that two moles of phosphorus atoms must be present for every mole of boron atoms in the compound.

Conclusion

In each of the experiments performed, reduction of phosphorus from the +5 oxidation state to the +3 oxidation state occurred. Although no specific kinetic studies were performed in the present project, it was observed that N,N-dimethylaminotriphenylphosphonium ion was reduced much quicker and more readily than iminotriphenylphosphorane. This is what would be expected based on the amount of $d\pi-p\pi$ overlap between phosphorus and nitrogen. The positively charged species would be expected to have the least amount of π -overlap and thus to be more reactive toward

reducing agents. Reduction of phosphorus is also observed in the high temperature decomposition of N-alkyliminotriphenylphosphorane boranes. It was also observed that dimethylaminoborohydride reduced N,N-dimethylaminotriphenylphosphonium ion faster than borohydride ion did.

In general, all of the reduction reactions occurred through attack of phosphorus by $B-H^-$ groups to form triphenylphosphine, protons and amino attached BH_n fragments. The amino $-BH_n$ fragments eventually reacted with protons to form amines or amine boranes. All of the reduction sequences produced a volatile amino compound. In order to explain the observed reaction products and their distributions, in the experiments involving reduction of N,N-dimethylaminotriphenylphosphonium ion, intermediate reducing agents must have been formed.

In the first reduction sequence studied, a base was initially present which should be a stronger base than triphenylphosphine. Thus, the diborane produced in the first sequence would attach itself to iminotriphenylphosphorane preferentially, and only a small amount of triphenylphosphine borane would be produced. Also, since neither iminotriphenylphosphorane borane nor ammonia borane were observed in the B^{11} nmr spectra, these compounds cannot have been in appreciable concentration long enough to exchange BH_3 with triphenylphosphine. This is probably due to the low thermal stabilities of these two materials. The other two aminoborohydride fragments would not be expected

to have exchanged BH_3 with triphenylphosphine because of the basicities of the amino groups.

The use of tetra-n-butyl-ammonium ion complicated the reduction of iminotriphenylphosphorane by borohydride. Several reaction products were the result of β -elimination reactions. The production of the new, quite unexpected compound, bis(iminotriphenylphosphorane) borane most likely proceeded from a β -elimination product.

In the second reaction sequence studied, no diborane was produced because dimethylaminoborohydride is a strong base. The second reduction sequence was a clean reaction with few side products. The products were easily identified, and as a consequence, the reaction sequence was easy to determine.

In the third reaction sequence studied, volatile dimethylamine was most likely produced. Since this product can leave the reaction solution, exchange of BH_3 between dimethylamine borane and triphenylphosphine would be shifted toward production of triphenylphosphine borane. Therefore, even though dimethylamine is a stronger base than triphenylphosphine, triphenylphosphine borane would be expected to be the predominant triphenylphosphine containing product. Since dimethylamine borane is more stable thermally than ammonia borane, the dimethylamine borane would be expected to be in appreciable concentration long enough to exchange BH_3 with triphenylphosphine. The reaction sequence was complicated by the occurrence of unidentified side reactions

and products. This particular reaction sequence requires more detailed study in the future to gain better understanding of the complicated chemistry involved and to identify the unknown products.

Phosphorus-31 and B¹¹ nmr spectroscopy provided a valuable tool to probe reactions with. The observation of these nuclei had the advantage of not having to use deuterated solvents. Thus, aliquots removed directly from the reaction mixtures were used to measure the progress of the reactions. The use of N,N-dimethylaminotriphenylphosphonium ion with borohydride and dimethylaminoborohydride made identification of most of the boron containing products quite simple. The borane chemistry of the dimethylamino group is well described and quite complete, including valuable B¹¹ nmr data. Use of these materials made the observation of some interesting boron-nitrogen chemistry possible.

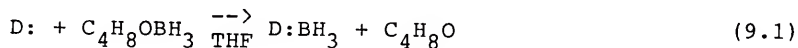
Finally, reduction of phosphorus in the N-substituted-iminotriphenylphosphoranes and their derivatives, provides a new reaction mode for these compounds, which before now had not been investigated.

CHAPTER IX

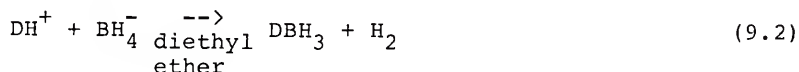
SUMMARY

A number of borane adducts of N-substituted-iminotriphenylphosphoranes were prepared in this study by two different general synthetic methods. Symmetrical boron cations containing N-alkyliminotriphenylphosphoranes as ligands were prepared using the appropriate borane adducts as starting materials. An investigation of the relative basicities of N-alkyliminotriphenylphosphoranes was conducted by measuring equilibrium constants for exchange of BH_3 . The amount of $d\pi-p\pi$ overlap in N-substituted-iminotriphenylphosphoranes and their borane adducts was measured by crystallographic and P^{31} nmr data. Reduction of iminotriphenylphosphorane and N,N-dimethylaminotriphenylphosphonium ion by different reducing agents was studied in detail.

The first method used for the preparation of borane adducts was displacement of tetrahydrofuran from its borane adduct by an N-substituted-iminotriphenylphosphorane according to the following equation



where D: = a N-substituted-iminotriphenylphosphorane. The second method employed in situ generation of diborane by reaction of N-substituted-aminotriphenylphosphonium bromides with lithium borohydride in diethyl ether according to the following equation



where D = a N-substituted-iminotriphenylphosphorane.

The procedure for the preparation of the symmetrical boron cations involved iodination of an appropriate phosphorane borane followed by nucleophilic substitution of the iodide group by the corresponding phosphorane. The preparation is represented by the following equations



where D = a N-alkyliminotriphenylphosphorane. An attempt to prepare the unsymmetrical cation, (trimethylamine) (N-n-propyliminotriphenylphosphorane) BH_2^+I^- , resulted only in the isolation of a mixture of symmetrical boron cations.

Physical, chemical and spectral properties of the borane adducts and boron cations, namely thermal and hydrolytic stabilities, infrared and nmr spectra, were described

in detail. In addition, stabilities of the boron cations toward silver (I) and borohydride ions were studied.

Equilibrium constants for the exchange of BH_3 between N-alkyliminotriphenylphosphoranes and borane adducts of trimethylamine and 4-methylpyridine were measured by integrating peaks in ^1H , ^{11}B and ^{31}P nmr spectra. It was found that all of the phosphoranes studied were less basic than trimethylamine. It was also found that the phosphoranes were less basic than 4-methylpyridine except when the alkyl groups were methyl, ethyl and n-propyl. The base strengths of the phosphoranes were found to decrease with an increase in the alkyl group size. The observed order in basicities was explained by a combination of steric and electronic factors.

The crystal structures of N-methyliminotriphenylphosphorane borane and N,N-dimethylaminotriphenylphosphonium tetrafluoroborate were measured. The P-N bond distances were compared to P-N bond distances in compounds having varying amounts of multiple bond character between phosphorus and nitrogen. It was found that there is less double bond character between phosphorus and nitrogen in the cation than in the borane adduct.

Phosphorus-31 nmr chemical shifts of N-substituted-iminotriphenylphosphoranes and their borane adducts were used to calculate the amount of π bonding between phosphorus and nitrogen in each molecule. The chemical shifts and

calculated group electronegativities were used in equations developed by Letcher and Van Wazer (48). In this manner the number of electrons in the $d\pi$ orbitals of phosphorus was calculated. The values were used to determine the change in π bonding on coordination to BH_3 . It was found that a decrease in π bonding is observed when a phosphorane is complexed by BH_3 .

Trends in the amount of π bonding were attributed to steric and electronic factors. A correlation between the amounts of π bonding and the relative basicities of the N-alkyliminotriphenylphosphoranes was made. The two methods used to determine the extent of multiple bonding, between phosphorus and nitrogen, were compared to each other.

Iminotriphenylphosphorane was reduced by tetra-n-butyl-ammonium borohydride to produce triphenylphosphine as the reduction product. A new compound was produced from the reaction and was identified as $[(\text{C}_6\text{H}_5)_3\text{PN}]_2\text{BH}$. The new compound was most likely produced through proton abstraction from the tetra-n-butyl-ammonium ion.

The compound N,N-dimethylaminotriphenylphosphonium iodide was reduced by lithium borohydride and sodium dimethylaminoborohydride in two separate experiments. Triphenylphosphine was the reduction product in both experiments. It was found that N,N-dimethylaminotriphenylphosphonium ion was reduced more easily than iminotriphenylphosphorane. The reactivity difference was attributed to the degree of π overlap.

APPENDIX

COMPUTER PROGRAM USED IN CALCULATION OF n_π FOR N-ETHYLIMINOTRIPHENYLPHOSPHORANE

This appendix contains a representative of the computer programs used for calculation of n_π values. The original version of this program, minus the line at 320, can be found in Reference 48.

Using MPZ_2T as a model, the various parameters in the program are defined as follows: XM, XT and XZ are the electronegativities of the M, T and Z groups respectively; EA stands for the MPZ bond angle, and EP stands for the MPT angle; DL stands for the P^{31} chemical shift; Z stands for α_1 ; NP stands for n_π .

```

10 XM = 2.476187
12 XZ = 2.49144
14 XT = XZ
20 EA = 110.7
22 EP = 114.6
30 DL = -3.559
50 HM = 1.0 + (0.16 * (2.15 - XM)
    ) + (0.035 * ((2.15 - XM) ^
    2))
60 HZ = 1.0 + (0.16 * (2.15 - XZ)
    ) + (0.035 * (2.15 - XZ) ^
    2))
70 HT = 1.0 + (0.16 * (2.15 - XT)
    ) + (0.035 * ((2.15 - XT) ^
    2))
80 CE = COS ((EA - 90.0) * 3.141
    5927 / 180.0)

```

```

90 CP = COS ((EP - 90.0) * 3.141
    5927 / 180.0)
100 CS = CE * CE
110 ST = 1.0 - CS
120 SE = SQR (ST)
130 TE = SE / CE
140 TP = TE * TE
150 CT = CP * CP
160 SP = 1.0 - CT
170 SZ = SQR (SP)
180 TZ = SZ / CP
190 TT = TZ * TZ
200 CF = (TE / (4.0 * TZ)) - ( SQR
    ((TP / (16 * TT)) + 0.5))
210 CZ = CF * CF
220 SS = 1.0 - CZ
230 SF = SQR (SS)
240 G1 = HZ / (2.0 * CS * SS)
250 G3 = HM * (((2.0 * CS * SS) -
    1.0) / ((2.0 * CS * SS) - CS
    ))
260 EP = HT / ((((( - CE * CP * C
    F) - (SE * SZ)) ^ 2) / ((2.0
    * CS * SS) - 1.0)) + 1.0)
270 S1 = HZ
280 S2 = (2.0 * G1 * CS * CZ) + (
    EP * CT)
290 S3 = (2.0 * G1 * ST) + (EP *
    SP) + G3
300 S4 = (( - 2.0 * G1 * SE * CE *
    CF) - (EP * CP * SZ))
310 Z = S1 + S2 + S3 - (0.5 * ((S
    1 * S2) + (S1 * S3) + (S2 *
    S3))) + (0.5 * S4 * S4)
320 NP = ((11828.5 - (7940 * Z) -
    DL) / 149)
330 PRINT "NP = "NP
335 PRINT "Z= "Z
340 END

```

REFERENCES

1. A.E. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N.Y., 1933, p. 51.
2. A.B. Burg and H.I. Schlesinger, J. Am. Chem. Soc., 59, 780 (1937).
3. H.I. Schlesinger and A.B. Burg, ibid., 60, 290 (1938).
4. A.B. Burg and R.I. Wagner, ibid., 76, 3307 (1954).
5. E.L. Gamble and P. Gilmont, ibid., 62, 717 (1940).
6. J.R. Elliott, W.L. Roth, G.F. Roedel and E.M. Boldebuck, ibid., 74, 5211 (1952).
7. S.G. Shore and R.W. Parry, ibid., 77, 6084 (1955).
8. M.A. Frisch, H.G. Heal, H. Mackle and I.O. Madden, J. Chem. Soc. (London), 899 (1965).
9. R. Koster, Angew. Chem., 69, 94 (1957).
10. E.C. Ashby and W.E. Foster, J. Am. Chem. Soc., 84, 3407 (1962).
11. H.C. Brown, H.I. Schlesinger and S.Z. Cardon, ibid., 64, 325 (1942).
12. H.I. Schlesinger, R.F. Sanderson and A.B. Burg, ibid., 61, 536 (1939).
13. G.W. Schaeffer and E.R. Anderson, ibid., 71, 2143 (1949).
14. K. Lang and F. Schubert, U.S. Patent 3,037,985 (1962).
15. K.C. Nainan and G.E. Ryschkewitsch, Inorg. Chem., 8, 2671 (1969).
16. W.J. Murphy, Chem. Eng. News, 30, 4515 (1952).

17. H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 2, 635 (1919).
18. H. Staudinger and E. Hauser, *ibid.*, 4, 861 (1921).
19. H. Zimmer and G. Singh, *J. Org. Chem.*, 28, 483 (1963).
20. H. Zimmer and G. Singh, *ibid.*, 29, 1579 (1964).
21. L. Horner and H. Oediger, *Liebigs Ann. Chem.*, 627, 142 (1959).
22. H. Zimmer, M. Jayawant and P. Gutsch, *J. Org. Chem.*, 35, 2826 (1970).
23. R. Appel and A. Hauss, *Chem. Ber.*, 93, 405 (1960).
24. H.H. Sisler, H.S. Ahuja and N.L. Smith, *J. Org. Chem.*, 26, 1819 (1961).
25. R. Appel and F. Vogt, *Chem. Ber.*, 95, 2225 (1962).
26. H. Zimmer and G. Singh, *J. Org. Chem.*, 29, 3412 (1964).
27. F. Kaplan, G. Singh and H. Zimmer, *J. Phys. Chem.*, 67, 2509 (1963).
28. S.G. Shore and R.W. Parry, *J. Am. Chem. Soc.*, 80, 8 (1958).
29. K.C. Nainan, Doctoral Dissertation, University of Florida (1969).
30. N.E. Miller, D.L. Reznicek, R.J. Rowatt and K.R. Lundberg, *Inorg. Chem.*, 8, 862 (1969).
31. S.G. Shore, C.W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, 87, 2755 (1965).
32. N.E. Miller and E.L. Muetterties, *ibid.*, 86, 1033 (1964).
33. J.E. Douglass, *ibid.*, 86, 5431 (1964).
34. J.E. Douglass, G.R. Roehrig and O. Ma, *J. Organomet. Chem.*, 8, 421 (1967).
35. G.E. Ryschkewitsch, *J. Am. Chem. Soc.*, 89, 3145 (1967).
36. K.C. Nainan and G.E. Ryschkewitsch, *Inorg. Chem.*, 7, 1316 (1968).

37. K.C. Nainan and G.E. Ryschkewitsch, J. Am. Chem. Soc., 91, 330 (1969).
38. M. Inoue and G. Kodama, Inorg. Chem., 7, 430 (1968).
39. H. Nöth, H. Beyer and H. Vetter, Chem. Ber., 97, 110 (1964).
40. G. Singh, Doctoral Dissertation, University of Cincinnati (1964).
41. G. Singh, in "Main Group Elements and Their Compounds," Methodicum Chemicum, Vol. 7, Part B, Academic Press, New York, N.Y., 1978, p. 529.
42. A.W. Johnson and S.C.K. Wong, Can. J. Chem., 44, 2793 (1966).
43. W.A.G. Graham and F.G.A. Stone, J. Inorg. Nucl. Chem., 3, 164 (1956).
44. D.P. Craig and N.L. Paddock, J. Chem. Soc. (London), 4118 (1962).
45. E. Hobbs, D.E.C. Corbridge and B. Raistrick, Acta Crystallogr., 6, 621 (1953).
46. P.A. Fowell and C.F. Mortimer, J. Chem. Soc. (London), 2913 (1959).
47. A.P. Claydon, P.A. Fowell and C.T. Mortimer, ibid., 3284 (1960).
48. J.H. Letcher and J.R. Van Wazer, in "³¹P Nuclear Magnetic Resonance," Topics in Phosphorus Chemistry, Vol. 5, Interscience Publishers, New York, N.Y., 1967, pp. 75-225.
49. V.D. Aftandilian, H.C. Miller and E.L. Muetterties, J. Am. Chem. Soc., 83, 2471 (1961).
50. A. Brandstrom, U. Junggren and B. Lamm, Tetrahedron Lett., 3173 (1972).
51. G.E. Ryschkewitsch and J.W. Wiggins, Inorg. Syntheses XII (1970).
52. H. Nöth and H. Beyer, Chem. Ber., 93, 2251 (1960).
53. E.R. Birnbaum, Doctoral Dissertation, University of Florida (1961).

54. V.E. Wiberg, A. Bolz and P. Buchheit, *Z. Anorg. Chem.*, 256, 285 (1948).
55. A.B. Burg and C.L. Randolph, Jr., *J. Am. Chem. Soc.*, 71, 3451 (1949).
56. K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Academic Press, New York, N.Y., 1965.
57. M.D. Taylor, L.R. Grant and C.A. Sands, *J. Am. Chem. Soc.*, 77, 1506 (1955).
58. J.A. Bigot, Th. J. De Boer and F.L.J. Sixma, *Recl. Trav. Chim. Pays-Bas*, 76, 996 (1957).
59. G.E. Ryschkewitsch, *J. Am. Chem. Soc.*, 82, 3290 (1960).
60. H.G. Heal, *J. Inorg. Nucl. Chem.*, 16, 208 (1961).
61. E.L. Muetterties, *Pure Appl. Chem.*, 10, 53 (1965).
62. L.W. Daasch and D.C. Smith, *Anal. Chem.*, 23, 853 (1951).
63. N.B. Colthup, *J. Optical Soc. Am.*, 40, 397 (1950).
64. H.R. Allcock, "Phosphorus-Nitrogen Compounds," Academic Press, New York, N.Y., 1972, p. 48.
65. R.C. Taylor, in "Boron-Nitrogen Chemistry," *Advances in Chemistry Series*, No. 42, American Chemical Society, Washington, D.C., 1964, p. 59.
66. A.R. Katritzky, *J. Chem. Soc. (London)*, 2049 (1959).
67. E. Stenhagen, S. Abrahamsson and F.W. McLafferty, "Registry of Mass Spectral Data," Vol. 2, John Wiley and Sons, New York, N.Y., 1974.
68. E. Stenhagen, S. Abrahamsson and F.W. McLafferty, "Registry of Mass Spectral Data," Vol. 1, John Wiley and Sons, New York, N.Y., 1974.
69. W.W. Paudler, "Nuclear Magnetic Resonance," Allyn and Bacon, Boston, Mass., 1974, p. 309.
70. J.A. Pople, W.G. Schneider and H.J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York, N.Y., 1959.
71. A. Saji, Master's Thesis, University of Florida (1961).
72. K.A.O. Starzewski and H.T. Dieck, *Inorg. Chem.*, 18, 3307 (1979).


73. W.D. Phillips, H.C. Miller and E.L. Muetterties, J. Am. Chem. Soc., 81, 4496 (1959).
74. D.E. Young, G.E. McAchran and S.G. Shore, ibid., 88, 4390 (1966).
75. M. Windholz, "The Merck Index," 10th ed., Merck and Company, Rahway, N.J., 1983.
76. A. Wilson and D. F. Carroll, J. Chem. Soc. (London), 2548 (1960).
77. M.W. Dougill, ibid., 5471 (1961).
78. M.J.E. Hewlins, ibid., 942 (1971).
79. J.E. Huheey, J. Phys. Chem., 69, 3284 (1965).
80. J. Hinze, M.A. Whitehead and H.H. Jaffe, J. Am. Chem. Soc., 85, 148 (1963).
81. J. Hinze and H.H. Jaffe, J. Phys. Chem., 67, 1501 (1963).
82. J.E. Huheey, J. Org. Chem., 31, 2365 (1966).
83. J. Hinze and H.H. Jaffe, J. Am. Chem. Soc., 84, 540 (1962).
84. K. Niedenzu and J.W. Dawson, ibid., 81, 5553 (1959).
85. K.A.O. Starzewski and H.T. Dieck, Phosphorus, 6, 177 (1976).
86. E. Wiberg and A. Bolz, Chem. Ber., 73B, 209 (1940).
87. H. Nöth and H. Vahrenkamp, ibid., 99, 1049 (1966).
88. A.B. Burg and C.L. Randolph, Jr., J. Am. Chem. Soc., 73, 953 (1951).
89. H. Nöth and H. Vahrenkamp, Chem. Ber., 100, 3353 (1967).
90. P.C. Keller, Chem. Commun., 1465 (1969).
91. B.M. Graybill and J.K. Ruff, J. Am. Chem. Soc., 84, 1062 (1962).
92. P.C. Keller, ibid., 91, 1231 (1969).
93. P.C. Keller, Inorg. Chem., 10, 1528 (1971).

94. D.F. Gaines and R. Schaeffer, J. Am. Chem. Soc., 86, 1505 (1964).

BIOGRAPHICAL SKETCH


William Keith Holley was born on September 15, 1960, at Roanoke County, Virginia. In June, 1978, he was graduated from J.H. Rose High School, Greenville, North Carolina. In December, 1982, he received the degree of Bachelor of Science with a major in chemistry from East Carolina University. From January, 1983, until the present time he has pursued his graduate work towards the degree of Doctor of Philosophy in the Department of Chemistry, University of Florida. During this period he worked as a teaching assistant in the Department of Chemistry.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.




George E. Ryschkewitsch,
Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



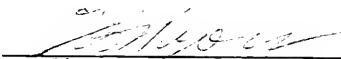
Harry H. Sisler
Distinguished Service
Professor Emeritus of
Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



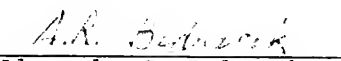
R. Carl Stoufer
Associate Professor of
Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Gardiner H. Myers
Associate Professor of
Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Alexander R. Bednarek
Professor of Mathematics

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1986

Dean, Graduate School

UNIVERSITY OF FLORIDA



3 1262 08553 4278